

The
LaQUE CENTER
FOR CORROSION TECHNOLOGY, INC.

**SEAWATER CREVICE CORROSION RESISTANCE OF
STAINLESS STEELS COATED WITH
SILANE AND ANTIFOULING PAINT SYSTEMS**

**FINAL REPORT
CONTRACT N00014-01-C-0177**

Prepared for

**Office of Naval Research
800 North Quincy Street
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Prepared by

**R. M. Kain
LaQue Center for Corrosion Technology, Inc.
702 Causeway Drive, P. O. Box 656
Wrightsville Beach, NC 28480**

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Robert M. Kain

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
LaQue Center for Corrosion Technology, Inc.
702 Causeway Drive, P. O. Box 656
Wrightsville Beach, NC 28480-0656

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13. ABSTRACT (Maximum 200 words)

Normally, stainless steel is utilized without any type of coating whatsoever. However, there are occasions where coatings may be contemplated. One of present interest to the U.S. Navy is that associated with the use of antifouling coatings on ship hulls fabricated of non-magnetic, austenitic stainless steel. Testing in natural seawater has demonstrated that coatings can protect susceptible stainless steel from barnacle related crevice corrosion and localized corrosion at weldments. However, coating defects and damage create new areas for crevice corrosion to initiate. As discussed in an earlier project report documenting contract N00014-97-C-0216, specimens of several grades of stainless steel were extremely susceptible to crevice corrosion when partially coated with epoxy alone, or when top coated with antifouling paints of the ablative-Cu and elastomeric types. The use of zinc-rich primers is known to enhance resistance to crevice corrosion, but their use raises other issues. Of chief concern is the possibility of liquid metal embrittlement if the stainless steel were ever heated above the melting temperature for zinc. This current project addresses the alternate use of organic silane type coatings. Ideally, silane would eliminate the need for a zinc-rich primer and the epoxy barrier coating. Current test results show promise when silane is applied as an ultra-thin film on 6Mo stainless steel. Additional testing is proposed to resolve potential problems when silane + ablative-Cu coated stainless steel is subjected to cathodic protection. Because of the apparent lack of insulation provided by the thin-film silane, cathodic disbondment of the topcoat has been observed.

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**SEAWATER CREVICE CORROSION RESISTANCE OF
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EXECUTIVE SUMMARY

A recent publication in *CORROSION* by A. J. Sedriks and P. J. Dudt (Vol. 1, 2001, pp. 84-91) described the current and proposed use of austenitic stainless steel ship hull construction and the benefits and limitations thereof. Two limitations cited for this class of materials are the inherent lack of antifouling properties and the sensitivity to liquid metal embrittlement. To overcome the issue of fouling susceptibility, the use of antifouling paint is necessary. Earlier testing performed under ONR contract No. N00014-97-C-0216 demonstrated that selected austenitic stainless steels are prone to crevice corrosion when traditional coating systems for ordinary steel hulls are employed.

Severe corrosion was found within six months on test samples partially coated with epoxy barrier paints and topcoated with either ablative-Cu or elastomeric type antifouling paint. According to Sedriks and Dudt, the issue of crevice corrosion susceptibility has been addressed by others by the use of sacrificial zinc-rich primer before the application of epoxy. It is the zinc presence that raises concerns about the possibility for liquid metal embrittlement when repair welding or high temperature cutting is employed.

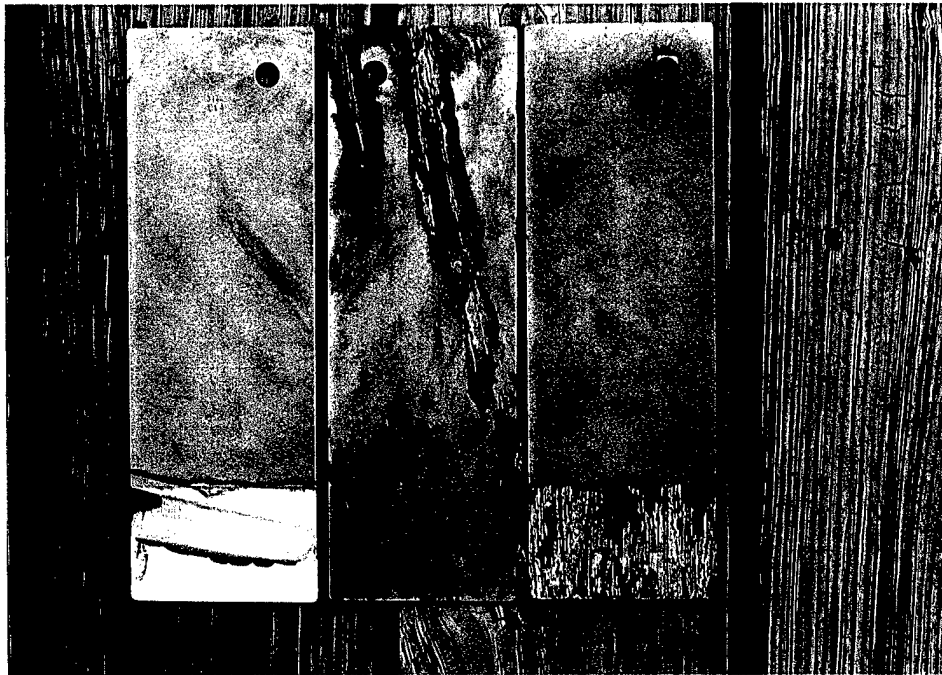
Current research is investigating the use of inorganic silane coatings as a pretreatment for the direct application of antifouling paint. The intent is to eliminate both needs for the epoxy coating and the zinc-rich primer. Working with researchers at the University of Cincinnati, the LaQue Center for Corrosion Technology, Inc. (LaQue Center) has conducted a nine-month seawater test program to investigate the benefits of silanes. This work has been conducted under ONR contract No. N00014-01-C-0177. In brief, testing comprised exposure of S31603 and N08367 stainless steels in the following conditions:

- controls partially coated 20% and 80% with a two layer epoxy system
- silane alone – three formulations applied to 20% and 80% coverage
- silane + ablative-Cu to the above coverages
- specimens fully coated with silane (three formulations) + ablative-Cu and scribed to introduce intentional defects
- repeat of the above fully coated specimens with zinc anodes

Preliminary results after three months of testing were previously reported to ONR under a cover letter dated January 7, 2002. That report included a technical paper presented at NACE CORROSION/2002 (Paper No. 02187) in Denver, CO. The present report gives full nine-month test results. The following conclusions were offered:

- Results of tests involving epoxy coated control specimens revealed attack, which closely approximated earlier results.
- S31603 was found to be susceptible to attack when coated with silane and topcoated with ablative-Cu antifouling paint.
- S31603 coated with silane alone was also susceptible to attack; however, the presence of silane did not promote the crevice corrosion observed on comparable epoxy coated specimens.
- All N08367 specimens coated with silane, with and without ablative-Cu, were fully resistant.
- While no attack was found on any specimen tested with zinc anodes, deterioration of the ablative-Cu resulted. Moreover, it was apparent that the thin film of silane did not electrically isolate the antifouling layer from the substrate.
- Figures ES-1 to ES-4 compare the resistance of the two alloys with the various coating schemes.
- Overall silane formulations A and B appeared more promising than formulation C.

Because of the problem observed under conditions of cathodic protection, some additional testing is envisioned. Proposed new tests would include the use of a thicker silane coating before the application of the antifouling coating, and the application of thin film silane prior to coating with epoxy and ultimately the antifouling Cu paint.



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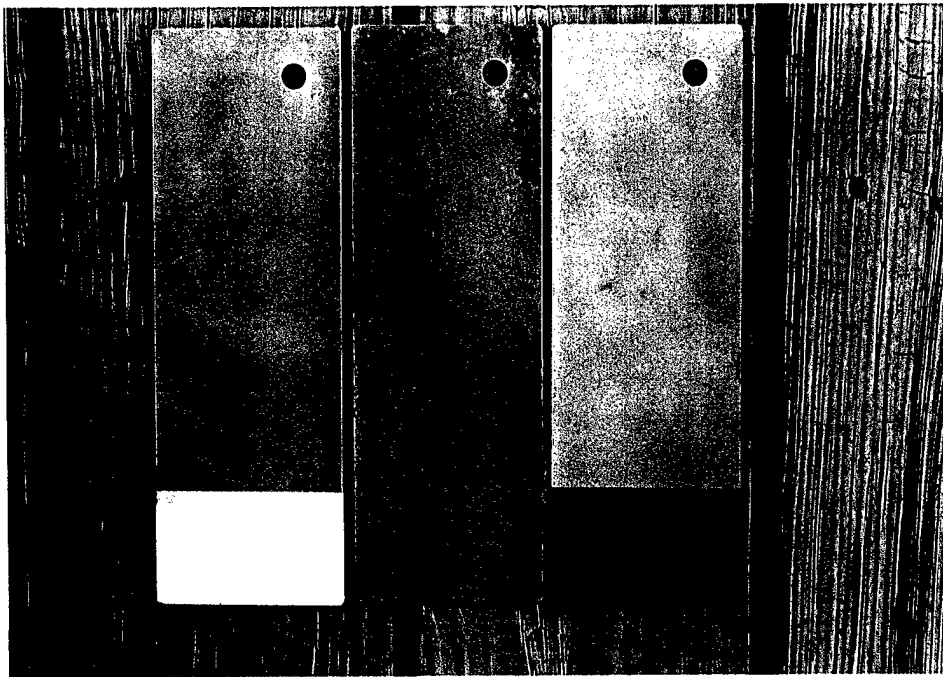
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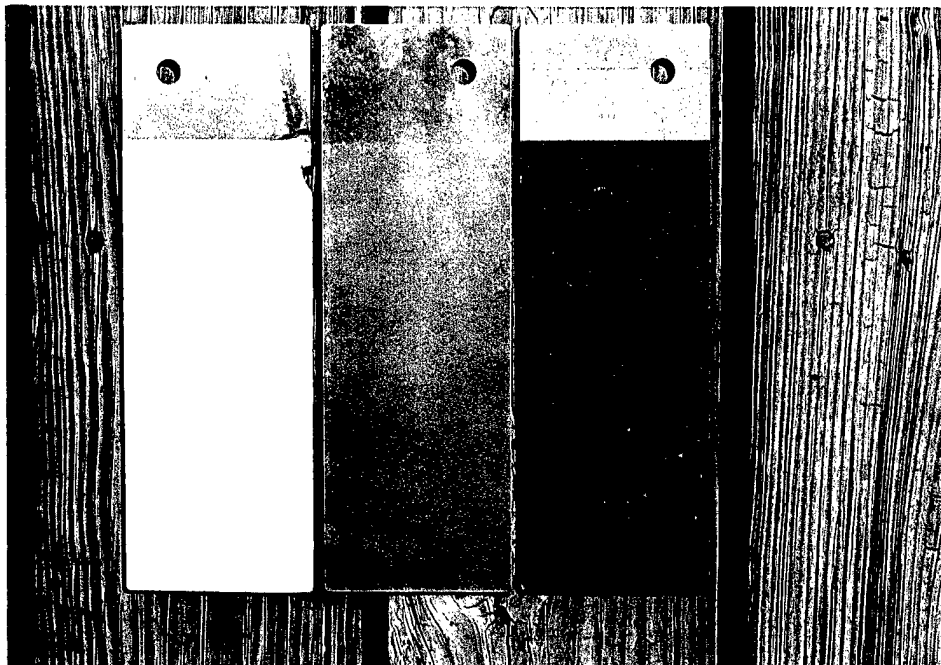
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Figure ES-1. Comparative views of S31603 specimens partially coated with (left-right) epoxy, silane alone and silane + ablative-Cu and exposed for nine months.



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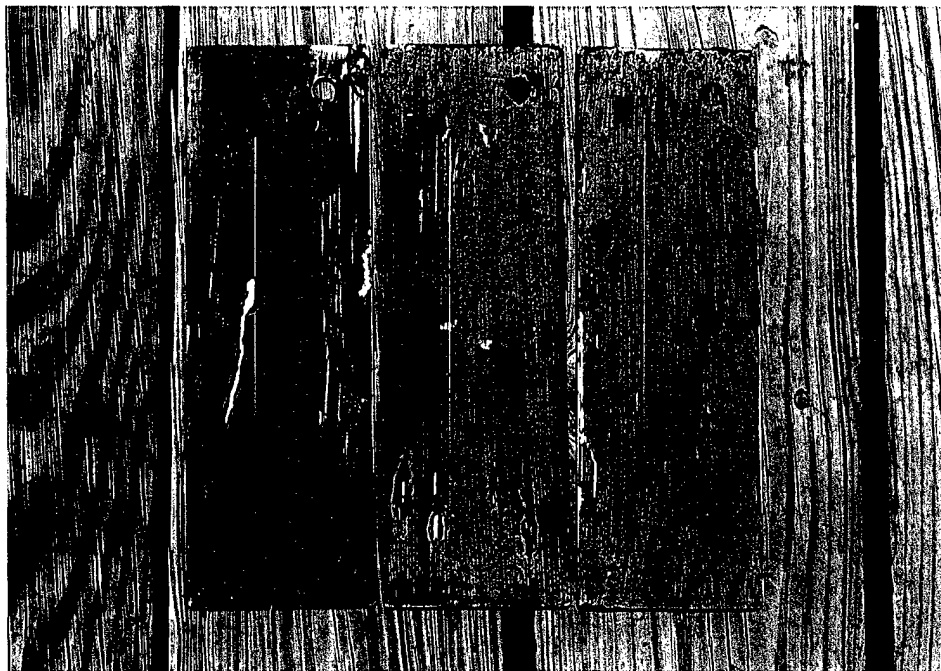
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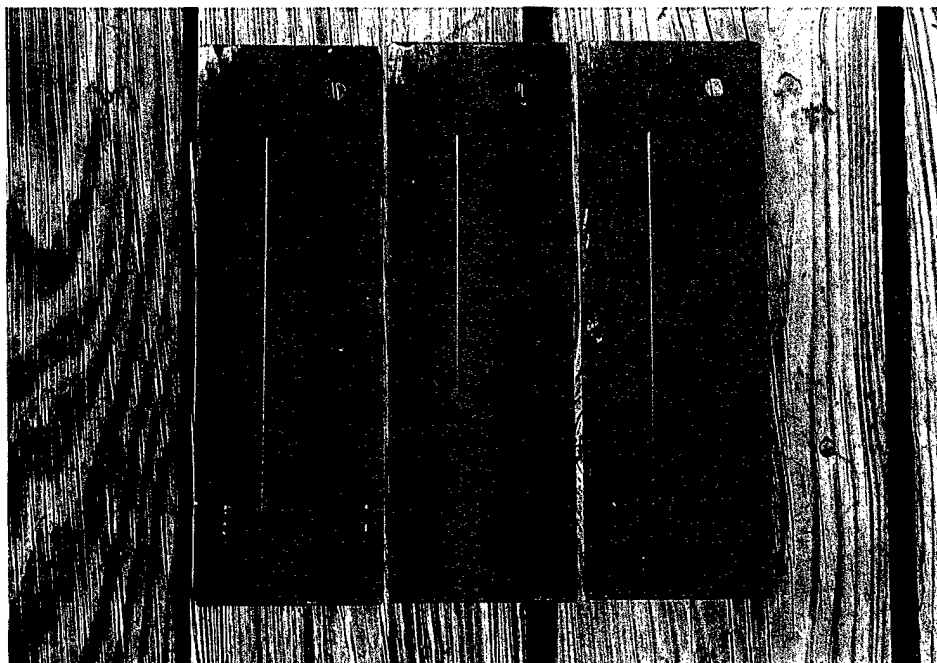
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Figure ES-2. Comparative views of N08367 specimens partially coated with (left-right) epoxy, silane alone and silane + ablative-Cu and exposed for nine months.



S31603

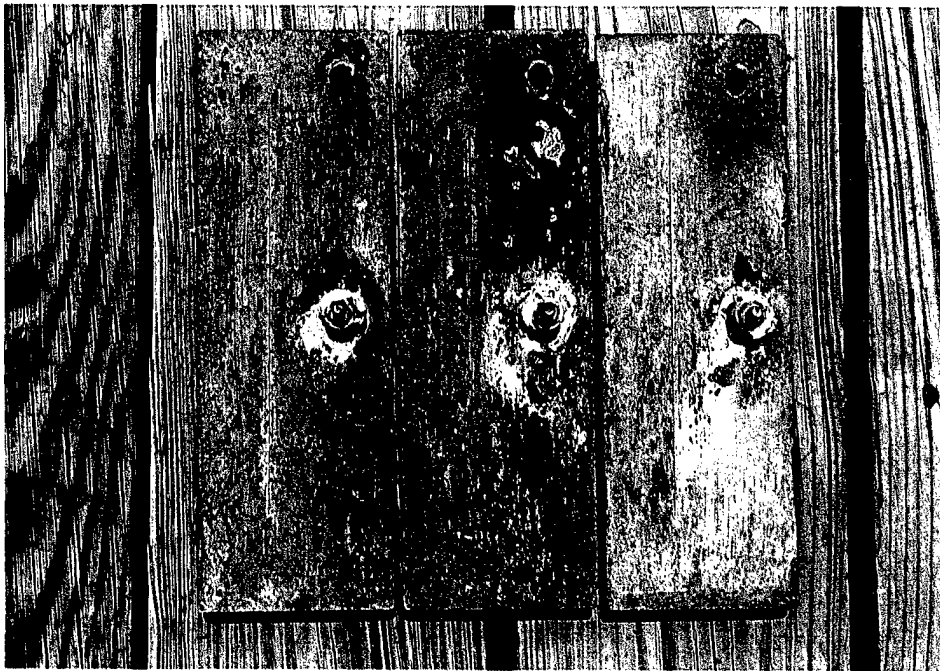
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N08367

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Figure ES-3. Comparative views of fully coated + scribed specimens exposed for nine months.
(Left-right: pretreated with Silane A, B and C)



2609-04-018-22

Figure ES-4. Representative view of fully coated + scribed specimens exposed for full nine months with zinc anode attachments.
(Shown N08367 (left-right) pretreated with Silane A, B and C.)

INTRODUCTION

While austenitic stainless steels have many attributes, their lack of inherent fouling resistance and the propensity for some grades to suffer crevice corrosion demand attention when designing for certain seawater applications. The potential use of austenitic stainless steels for ship hull applications, for example, has generated interest in investigating the influence of coatings on the fouling and crevice corrosion resistance of select grades including S31603, S20910 and N08367.¹⁻⁴

In the absence of antifouling protection, localized corrosion associated with barnacle growth can affect the 300 series alloys and others.^{5,6} As a general guide, those stainlesses with less than 6 percent molybdenum are the most likely to be attacked.⁷ While antifouling coatings can prevent or largely limit attachment by barnacle and other macrofoulers, coatings may serve as crevice formers in their own right. Previous work, for example, has shown that the above mentioned grades can be susceptible to crevice corrosion at coating to bare metal sites.^{2,3} As reported, epoxy coated stainless steel and epoxy + antifouling topcoated stainless steel were significantly affected when tested with large areas of bare metal, e.g., 20% and 80%. In contrast, fully coated test panels with intentionally scribed defects exhibited comparatively little attack in tests lasting up to one year.

As recently described by Sedriks¹, the use of a zinc-rich primer paint beneath the initial coat of epoxy cover has been employed to mitigate the chances for crevice corrosion at scratches and larger damage sites. One concern about the use of zinc-rich primer is the potential for liquid metal embrittlement of the stainless steel should the need for repair welding or high temperature cutting arise.^{1,8-10} Because of this added consideration, alternative coating systems to replace the zinc primer are being investigated.¹ Those covered in the present report are based on experimental organic silane formulations comprising 1:5 mixtures of vinyltriacetoxysilane (VTAS) and bis-amino silane.^{11,12} Existing antifouling paints of the ablative copper (Cu) and high surface energy elastomeric types are traditionally used in conjunction with epoxy undercoats.^{1,2} On steel hull vessels, the epoxy serves as a corrosion barrier coating. Ideally, the subject silane coatings would eliminate the need for both the zinc-rich primer, and the epoxy

barrier coating when applying antifouling paint to stainless steel. Some reported advantages of silanes include: environmental friendliness, process control, excellent adhesion between metals and other paint, ultra- thin films and anticorrosion performance.^{11,12}

Under contract with the Office of Naval Research, the LaQue Center for Corrosion Technology, Inc., (LaQue Center) has conducted a nine-month seawater test program to investigate any benefits derived by precoating stainless steel with silane prior to the direct application of a commercial ablative-Cu antifouling paint. A previous interim report (dated 1/7/02) and a related technical paper presented at NACE CORROSION/2002¹³ detailed the preparation of 240 stainless steel test specimens and provided results for 120 specimens removed after three months exposure. In brief, the project investigated the performance of Type 316L (UNS S31603) and 6Mo alloy AL6XN (UNS N08367) when coated with three different silane formulations developed by researchers at the University of Cincinnati's Department of Materials Science and Engineering and topcoated with a commercial antifouling paint (Interveron BRA640). Control specimens prepared with silane alone and others with a dual coating of epoxy, which produced significant attack on both alloys in earlier tests, were also exposed.

This final report highlights key aspects of the test design, details test procedures and conditions, and presents nine-month test results.

EXPERIMENTAL

Test Materials

Table 1 gives the chemical compositions for the UNS S31603 and UNS N08367 sheet materials tested in the present program. Also provided for comparison are the specification ranges for both materials.

From Table 1, it can be seen that the composition of the presently tested materials fell within the UNS specification ranges. In the case of S31603, the actual amounts of Cr, Ni and Mo are at the lower ends of the specification range. The same is true for the Cr content in N08367.

A comparison of the presently tested materials/compositions with those for like alloys tested earlier can be found in the referenced interim report (a revised version of the cited CORROSION/2002 paper appears in Appendix 1).

Overview of Procedure

Details concerning test specimen preparation, coating formulation and application are found in the interim report and in the attached Appendix 1. Initially, a total of 120 coated specimens of each alloy were prepared (Table 2) and ultimately exposed in five test tanks. Two tanks contained six replicates (3 in each tank) of the silane alone with epoxy coated specimens. Two other tanks contained six replicates of all freely corroding silane + ablative copper coated specimens. Finally, the fifth tank contained all six replicates of the silane + ablative copper coated specimens exposed with zinc anodes. The diagram in Figure 1 details the specimen deployment.

Following three months exposure, one set of triplicates of each coating variation was removed and evaluated while the remainder continued on exposure for an additional six months. The three-month removal activity emptied Tanks 1 and 2, and reduced the number of zinc protected specimens in Tank 5 by 50 percent. Specimens in Tanks 3 and 4 were not disturbed in any way.

Environmental

Throughout the nine-month test period, the filtered (5-10 μm) seawater refreshment and tank temperatures were monitored/adjusted three times daily (once/8-hour shift), 7 days a week. The average tank refreshment rate was 1.5 l/min. (0.4 gal/min) which equates to 4 to 5 complete volume changes daily. Results of source seawater (Banks Channel, Wrightsville Beach, NC) hydrology are provided in Table 3. As indicated, key parameters were analyzed or determined weekly, and the remainder monthly. The nine-month averages shown in Table 3 are within the range of data for the recent most 10 years analyses presented earlier in reference 13.

As shown in Table 4, the average temperature of seawater in the five test tanks fell within

the target range of $25^{\circ}\text{C} \pm 5^{\circ}\text{C}$. During the course of testing, some brief excursions below (min. 18.0°C) and above (max. 33.0°C) the target range were experienced. Based on the nearly 3,000 temperature measurements recorded, approximately 4 percent were out of the target range. The longest excursion (one-day) on the high side was recorded for Tank 4 that contained the silane + Cu coated specimens schedule for nine months exposure.

In-situ Inspections

As described in the interim report¹³, in-situ inspections were performed regularly during the initial three months of testing. Subsequently, the frequency of these inspections was reduced to monthly and bi-monthly.

Corrosion Potentials

With the aid of a pointed alloy 625 (shielded except for its tip) probe, a silver-silver chloride (Ag/AgCl/ Seawater) reference electrode and a high impedance digital voltmeter, the corrosion potential of each specimen was measured immediately prior to removal. These measurements were performed for specimens removed after both three months and nine months exposure periods.

Post-test Procedure

Upon removal from the test tanks, photographs depicting representative views of the specimens were taken before and after bristle brushing and fresh water rinsing. Subsequently, the partially coated specimens were acid cleaned to remove calcareous deposits which formed on the uncoated surfaces of those which incurred extensive localized corrosion.

For each affected specimen, the location and extent of attack was documented. The originally coated area affected by corrosion was quantified, as was its depth. The depth of non-coating related attack, which had developed, on the surfaces of S31603 specimens in both three-month and nine-month tests was also quantified. (Note these three-month test data were not included in the interim report).

RESULTS AND DISCUSSION

In-situ Inspections

Controls

As indicated in the interim report¹³, crevice corrosion was documented at all 24 primary sites (coating to bare metal interface) on the epoxy coated S31603 controls within 21 days. This constituted all sites on the specimens scheduled for three months and nine months exposure. In contrast, by the time of the three-month removal, attack of the corresponding N08367 was limited to only 5 of the 24 primary sites. In the case of N08367, the above attack was detected between 21 and 42 days, and was located on specimens scheduled for three months testing. (Subsequently, during final evaluation of the three-month specimens, a sixth affected site was detected.)

During the final six months of testing, two additional sites of attack were noted on the remaining epoxy coated N08367 specimens, one specimen each with 20% and 80% coverage. These observations were recorded after approximately seven months exposure. A possibility exists that these affected sites initiated earlier in the test, but went undetected due to poor visibility, and/or because of the relatively small amount of generated corrosion product, at least initially.

Silane Coated Specimens (with and without ablative-Cu)

Based on in-situ inspection results, all other freely corroding N08367 specimens, i.e., those with silane alone, and those with silane + ablative-Cu were apparently resistant for the full nine months.

In contrast to the resistance described above, many of the freely corroding S31603 specimens with silane alone, and silane + ablative-Cu exhibited attack within days and a few weeks of exposure. By the time of the scheduled three-month removal, all exhibited attack to some degree or another. This included those scheduled for three month and nine month removal. For those with silane alone, a considerable amount of attack initiated on the bare surfaces, often at the cut edges.

Cathodically Protected Specimens

Deterioration, initially discoloration and later disbondment and flaking, of the ablative-Cu coating on the S31603 and N08367 specimens in test with zinc anode protection was detected within a few days. Likewise, expected corrosion of the anodes developed quickly. While not previously mentioned, a black film (presumably copper related) developed on the exposed surfaces of the stainless steel (S31603) fasteners connecting the anodes to the specimens. Throughout the nine-month period, no evidence of "rust" was detected on any of the cathodically protected specimens.

In-situ Documentation

Figures 1.1 to 1.3 in Appendix 2 provides a series of photographs showing the in-situ appearance of the specimens remaining in Tanks 3, 4 and 5 for the full nine months. Figures 2.1 and 2.2 document the two affected sites found on the two epoxy coated N08367 specimens described above.

Corrosion Potentials

Table 5 summarizes the collected corrosion potential data for the various S31603 and N08367 specimens tested for three and nine months. These data have been arranged in a "galvanic series" with the most noble and most active values at the top and bottom, respectively. Published potential data for copper and zinc metal found, for example, in references 14 and 15, have been included for comparison. As indicated, the resistant N08367 specimens exhibited the most noble potentials. However, differences are observed between those with and without the ablative-Cu present. It remains uncertain if the differences observed are related to a galvanic effect related to copper (which is more active to stainless steel), or to differences in biofilm influenced by dissolved copper in the seawater, or perhaps to both. Note that in the copper-free tank, resistant N08367 specimens tested with epoxy and silane alone exhibited potential in excess of +0.450 V after nine months. These are among the most noble potentials ever recorded for stainless steel at the LaQue Center. According to Professor S. Dexter (University of Delaware, Department of Marine Science)¹⁶, potentials approaching this range have been documented in other coastal waters¹⁷, and are within the theoretical range proposed earlier by

More active potentials for the attacked S31603 and N08367 specimens reflect mixed potentials influenced by the actively corroding areas and the resistant cathodic areas. Whereas, the potentials for the resistant N08367 specimens became more noble during the last six months of testing, those for the corroding S31603 and N08367 either remained about the same or became somewhat more active.

Potential data for the cathodically protected specimens again reflect some mixed potential attributed to the corroding zinc anode and the behavior of the ablative-Cu coated stainless steel. The observed increase (more positive) with time is likely indicative of anode wastage. The potentials shown in Table 5 for these cathodically protected specimens are more active than those considered necessary for the protection of stainless steels. Moreover, suppression of the potential of copper could negate its antifouling characteristics. In the absence of macrofouling in the filtered seawater tests, questions remain as to whether or not the antifouling characteristics of the copper paint had actually been negatively influenced.

As-removed Appearance

Photographs in Figures 3.1 to 9.3 in Appendix 2 provide representative as-removed views of the various S31603 specimens following nine months of continuous exposure. The letter designations F or B denote the front (code side) or back side of the indicated specimens. Extensive corrosion is clearly visible on the partially coated specimens. Somewhat less attack is shown for the fully coated + scribed specimens exposed without zinc anode protection. In addition to the obvious corrosion product, the specimens were found to be covered with marine slime and "floc" generated by the developed corrosion product. In addition, the exposed base metal portion, which is cathodic to the crevice area, of the partially coated specimens was covered with calcareous deposits to some extent or another. This deposition is more clearly observed on the surface of the brush and water cleaned specimens shown, for example, in Figure 3.3. During the course of subsequent acid cleaning, all 24 of S31603 specimens with epoxy and silane alone exhibited substantial effluence, indicative of calcareous deposition.

Corresponding as-removed views of the various N08367 specimens are shown in Figures 10.1 to 16.3. Only two of N08367 specimens exhibited accumulations of corrosion product (Figures 10.1 and 10.2). Again, these were the two specimens partially coated with epoxy and previously shown in-situ in Figures 2.1 and 2.2. While marine slimes and "floc" were noted, there was little evidence of calcareous deposition except for one of the affected epoxy coated specimens with 80% coverage (No. 118).

In the absence of stainless steel corrosion of the protected specimens in Tank 5, there was no "floc" present on the surfaces of the S31603 and N08367 specimens (Figures 9.1 to 10.3, and 16.1 to 16.3, respectively). However, what is clearly observed is the previously mentioned deterioration of the ablative-Cu coating and the differences thereof. Also shown in the preceding Figures is the buildup of white corrosion product associated with the sacrificial zinc anodes. (NOTE: Figure page 17 intentionally left blank.)

After-cleaning Assessment

Epoxy Coated Specimens

Figures 18.1 to 32.1, in Appendix 2, show the condition of the various specimens following cleaning and removal of the coating(s) loosened by the underlying corrosion.

Figures 18.1 and 18.2 (20%), and Figures 19.1 and 19.2 (80%) show the extent of crevice corrosion which developed beneath the epoxy coating on S31603 specimens in nine months. Figures 18.3 and 19.3, respectively, compare the "worst case" condition of the preceding with that found on corresponding specimens removed after only three months.

Figures 20.1 to 21.3 show corresponding views of the epoxy coated N08367 specimens. While the in-situ inspections revealed only two affected sites, the final inspection revealed a continuation of attack on the opposite sides of the respective specimens; thus bringing the total number of affected N08367 sites on the nine-month specimen to four. As can be seen from Figure 20.3, the most severe attack among the N08367 specimens occurred on one of those exposed for three months with 20 percent coverage.

Table 6 summarizes the incident of attack incurred by both stainlesses in the present and earlier tests. While S31603 exhibited a "failure" rate of 100 percent, the overall rate for N08367 was only about 50 percent. This behavior is consistent with the expected resistance associated with high alloy content in N08367. As reported previously¹³ the Cr + 3.5xMo + 16xN equivalent for the present heats of S31603 and N08367 are 23.85% and 44.69%, respectively. In other words, the nearly two-fold increase in the equivalent value for N08367 resulted in a 50 percent reduction in the incident of attack, as compared with S31603.

Affected Area

Tables 7 and 8 give the measurements (cm^2) for affected areas beneath the epoxy coating on S31603 and N08367 specimens in the three-month and nine-month tests, respectively. These results are further summarized (as percent affected area) in Table 9. Included are results from the earlier six-month test.

From the data shown in Table 9, it can be seen that mean value for percent affected area was consistently lower for N08367 specimens than for S31603. In addition, the mean value was consistently lower for those specimens with 80% coverage than with 20% coverage. In the current tests, S31603 specimens exhibited an increase in the mean value upon longer exposure. Results from earlier tests with 80% coverage, but not 20% coverage, also fit this trend. On the other hand, the mean percent affected area incurred by N08367 specimens (20% and 80% coverage) appears to be independent of test duration. In the case of N08367, differences in times to initiation could account for the measured differences in affected area. It is recalled that while some attack of some three-month specimens was observed within 21 to 42 days, initiation of the nine-month specimens may have taken longer.

Depth of Attack

Tables 10 and 11, respectively, provide maximum depth of attack data for S31603 and N08367 specimens, which were partially coated with epoxy and exposed for three months and nine months, duration. These results are further summarized in Table 12. As can be seen, the absolute and mean values for both alloys in the current test with 20% coverage increased with the

longer exposure time. For tests with 80% coverage, only the mean value for S31603 specimens shows this affect. Absolute and mean values for maximum depth are shown to be consistently lower for N08367 than for S31603. However, as shown earlier (Table 11 versus Table 10), some N08367 depth of attack data fell within the range measured for S31603.

When considered with the earlier six-month test results, the maximum depth appears largely independent of duration. The one noted exception is for N08367 with 20% coverage.

The apparent absence of consistent trends from data in the current three-month and nine-month tests and the earlier six-month test may be accounted for by the following:

- Differences in heat chemistries
- Present tests comprised grit blasting of both surfaces, whereas only one surface was grit blasted in the earlier test.
- Epoxy was spray applied in the earlier test and brush applied in current tests.

Silane Alone

After-cleaning (to remove most of the corrosion products and calcareous deposition) views of each set of triplicate. S31603 and N08367 specimens partially coated with silane and exposed for a full nine months are shown in Figures 22.1 to 25.3.

All 18 of the silane coated (20% and 80%) S31603 specimens exhibited pitting/tunneling type attack, both within and outside the areas coated. As depicted in Figures 22.1 to 23.3, the attack sometimes originated at the exposed metal edges and elsewhere on the primary test surfaces. As can be seen, the presence of the ultra-thin silane coating did not promote the more classical type of crevice corrosion incurred by the previously discussed epoxy coated specimens shown, for example, in Figure 18.1. From the condition of these S31603 specimens, it is apparent that some of the propagation was influenced by gravity.

In contrast to the above, final inspection of the 18 partially coated N087367 specimens (Figures 24.1 to 25.3) revealed no evidence of corrosion within the areas coated (20% and 80%)

with any of the three silane formulations. Likewise, no evidence of localized corrosion was found on any of the boldly exposed specimen surfaces.

Depth of Attack

While the preceding interim report documented the above attack, quantification of the depth of attack was postponed until the conclusion of the nine-month test. Table 13 lists the maximum depth of the pitting/tunneling attack data for the S31603 specimens partially coated with silane as exposed for three and nine months duration. As indicated, a number of specimens exhibited perforations, resulting from attack on both sides. This generally occurred near the top of the panel where attack had originally initiated at a site on its edge section.

Penetration results are summarized in Table 14. In calculating the mean value of maximum depth for perforated S31603 specimens, one-half the panel thickness (1.5 mm) was used as the numerical input.

In the three-month test, depth of attack data suggests the greatest resistance for specimens treated with Silane formulation A at 80% coverage. Following nine-months of testing, those treated with Silane formulation C at 80% coverage appeared only modestly more resistant than those treated with either formulations A or B.

Stainless Steels Partially Coated with Silane and Ablative-Cu

Initiation Resistance

S31603 - All 18 partially coated S31603 specimens in both the three-month and nine-month test exhibited some degree of attack. As shown, for example, in Figures 26.1 and 26.2 (worst case example in nine-month test), this attack was largely confined to the coated areas. Unlike those coated with silane alone, attack of the boldly exposed surfaces was minimal, if at all. Figure 26.3 (discussed later) shows the appearance of the corresponding, fully coated + scribed specimen.

N08367 - In contrast to the above, all 18 of the partially coated N08367

specimens were fully resistant to attack in the present nine-month test. Likewise, all 18 in the related three-month test were also fully resistant. Figures 27.1 and 27.2 show the representative appearances of those in the nine-month test. Fully coated + scribed specimens are shown in Figure 27.3.

Propagation Resistance – Affected Area

Table 15 gives affected area data for the above group of partially coated S31603 specimens from the three-month and nine-month tests. Results are further summarized in Table 16, which includes maximum and mean percent values, and the calculated standard deviation (STD). Also indicated is the actual maximum value (cm^2) of the greatest affected area. From these data, it appears that specimens pretreated with Silane formulation C consistently exhibited the most attack. Among those tested with 20% coverage, specimens pretreated with Silane A exhibited the least attack. On the other hand, specimens with 80% coverage comprising Silane formulations A and B exhibited comparable resistance. Observe that both the actual values and the percent values for those pretreated with Silane formulation A and B are lower with 80% coverage than with 20% coverage. In the case of those pretreated with formulation C, the actual values (max.) are higher with 80% coverage than with 20% coverage.

The most significant impact of test duration is shown for those pretreated with Silane A at 20% coverage and those with Silane C at 80% coverage. Considering repeatability of results among the triplicate specimens, those prepared with formulation A were the most consistent overall. Figures 28.1 to 29.3 compare worst case examples of attack on the partially coated S31603 specimens in the three-month and nine-month tests.

Unlike the epoxy coated specimens (Figure 18.3) which show the progression of the attack from the primary coating-to-bare metal interface downward, the attack incurred by the S31603 silane + ablative-Cu coated specimens, at least those with 20% coverage (Figure 28.1), appears to have propagated upward. As shown in Figures 29.1 to 29.3, it appears that the location of the attack on those with 80% coverage is more random. Figures 30.1 to 30.3 provide close-up views of the attack affecting S31603 specimens.

Depth of Attack

Table 17 gives the maximum depth of attack measured within the coated areas of the above S31603 specimens. Again, all N08367 specimens were fully resistant. Results are further summarized in Table 18. For specimens exposed with 20% coverage for three months, those pretreated with Silane C exhibited the least amount of penetration (max. and mean value) and the least variability. Results for those exposed with 80% coverage show improvement in the mean value ongoing from Silane formulations A, to B, to C. Otherwise, there are no consistent trends observed. Increasing the test duration resulted in deep penetration for all combinations of formulation and percent coverage. In a number of cases, perforation of the 3mm sheet material resulted from attack propagating inward from both surfaces.

From Tables 17 and 18, it is observed that specimens pretreated with Silane C at 20% and 80% coverage exhibited the greatest mean value for affected area and the least mean value for depth in the three-month test. The same held true for those with 80% coverage in the nine-month test.

Stainless Steels Fully Coated with Silane + Ablative-Cu and Exposed with Scribed Defects

Initiation Resistance

S31603 - All eighteen of the fully coated + scribed specimens in this nine-month test exhibited some evidence of attack at the scribed area, and/or elsewhere. Comparative (worst case) views of three-month and nine-month fully coated + scribed S31603 specimens are provided in Figures 31.1 to 31.3. Note in Figures 31.2 and 31.3 that much of the original ablative-Cu had converted to "green copper" in the nine-month test. Figure 32.1 provides a close-up view of the attack incurred at the scribe on one of the Silane A pretreated specimens. Other views are included in the Appendix 1 report.

N08367 - No evidence of corrosion at the scribed defects, or elsewhere, were detected during the final inspection of the nine specimens exposed for each of the two test durations. A representative view of these resistant specimens was shown earlier in Figure 27.3. As shown in Figures 27.1 to 27.3, there was little or no conversion of the antifouling coating to

“green copper”, as was the case with corresponding S31603 specimens.

Affected Area

In the three-month test, at least one of six surfaces on the fully coated specimens pretreated with Silane Formulations A, B and C remained resistant.

For those removed after a full nine months, all surfaces showed some measure of attack; however, the percent area affected was limited to the range of <1% to 3%. Results summarized in Table 19 suggest little or no effect of silane formulation on this assessment parameter.

Depth of Attack

After three months of testing, the deepest penetration (0.22 mm) was measured remote to the scribe on S31603 specimen No. 022 which had been pretreated with Silane formulation A. After nine-months of testing, another Silane A treated specimen (No. 025) also exhibited the deepest penetration (2.28 mm). Results are summarized in Table 20. Based on the absolute maximum depth and the mean value of the maximums, specimens pretreated with Silane C exhibited the least penetration in both the three-month and nine-month tests. Considering only the mean values, similar trends in penetration resistance are observed in the three-month tests comprising fully coated + scribed specimens, and those for the partially coated specimens. Results suggest a similar trend in the nine-month tests for fully coated + scribed specimens and those with 80% coverage.

Stainless Steels Fully Coated with Silane + Ablative-Cu and Exposed with Scribed Defects and Cathodic Protection

Figures 32.2 and 32.3 show representative views of the cathodically protected S31603 and N08367 specimens, respectively. All 18 specimens showed considerable wastage of their zinc anodes and, as expected, no evidence of substrate corrosion. On the other hand, varying degrees of ablative-Cu coating degradation and calcareous deposition was observed. Both the extent of coating degradation and the mineral deposition was appreciably greater on the nine-month specimen than those removed earlier at three months. Figure 33.1 and 33.2 show close-up views of the scribed areas on non-protected and cathodically protected N08367 specimens,

respectively.

Under the previous contract, stainless steel test panels were initially coated with a two layer (grey over red) paint system and then topcoated with ablative-Cu. Zinc anodes were attached in the same fashion as described herein. Replicates were then exposed "overboard" for one year under conditions intended to promote heavy fouling on control panels. Except for some marine slime, the cathodically protected specimens continued to exhibit their intended fouling resistance. Some evidence of coating blistering was detected on controls (epoxy only) and those with the antifouling ablative-Cu topcoat. An example of the latter is shown in Figure 33.3. Other specimens prepared with an elastomeric type antifouling topcoat also experienced some blistering.

SUMMARY AND CONCLUSION

As part of ongoing research into the successful use of austenitic stainless steels for non-magnetic ship hull construction, a nine-month seawater test program has been conducted to evaluate any benefits in the use of silane coatings as a pretreatment to the application of antifouling paint. Earlier investigations had demonstrated that candidate stainless steels were prone to crevice corrosion when partially coated with epoxy and top coated with ablative-Cu and elastomeric type antifouling paints. While inorganic zinc primers have been successfully used to mitigate crevice corrosion, concerns about liquid metal embrittlement has promoted these investigations in the use of alternate coatings. Ideally, silane would eliminate the need for both, zinc and epoxy coatings. Reportedly, the silane pretreatment improves the bond between the principal coating and the substrate and provides corrosion protection.

The current work comprised exposure of 240 test specimens for up to nine months. In addition to epoxy coated controls, specimens were tested with three different formulations of silane, both with and without ablative-Cu top coats. While some specimens of the candidate materials, N08367 and S31603, were partially coated, others were fully coated (silane + ablative-Cu) and intentionally scribed to introduce coating "defects". These latter type specimens were

tested both with and without cathodic protection as afforded by zinc anodes. Interim three-month test results were presented at CORROSION/2002 in Denver, CO.

Based on final evaluation of the three-month and nine-month test specimens, the following observations and conclusions are presented.

- As in the previous tests, control specimens of both alloys were high susceptible to crevice corrosion when partially coated with epoxy.
- All N08367 specimens tested with silane alone (@ 20% and 80% coverage), silane + ablative-Cu (@ 20% and 80% coverage), silane + ablative-Cu (@ 100% coverage) + scribed were fully resistant.
- All S31603 specimens in the above conditions were susceptible to corrosion. However, the use of silane alone did not promote the crevice corrosion encountered by the epoxy coated specimens.
- S31603 specimens partially coated with silane alone exhibited extensive pitting and related tunneling attack on bare and coated specimens. This type of attack was largely mitigated by the ongoing crevice attack on epoxy coated specimens and those coated with silane + ablative-Cu.
- Fully coated S31603 specimens incurred generally superficial to mild attack at the intentional defect and elsewhere. The extent of attack was more or less proportional to the amount of bold surface (cathodic area) available.
- All cathodically protected specimens were fully resistant to attack, but extensive deterioration of the ablative-Cu was encountered. This can be attributed to polarization caused by the anodes which were enabled by the thin film silane's lack of insulating qualities.
- Because some areas of non-magnetic ship hulls are likely to receive cathodic protection, e.g., stern area, the observed antifouling coating deterioration generates a need for some additional investigation.

RECOMMENDATIONS

- Alleviation of the antifouling coating polarization issue may be addressed by (1) applying silane as a thicker, and hence more non-conductive, coating and (2) applying silane, as a thin film, prior to coating with epoxy.

- Ideally, both approaches will prove successful and thereby provide alternative coating schemes. Even if only one approach is proven successful, the need for the potentially problematic zinc-rich coating can be avoided.

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DISCLAIMER

It is understood that the information contained herein applies to the specific conditions of the work described in this document. Any extrapolation to other applications is beyond the scope of this effort.

TABLE 1

Chemical Composition of Stainless Steels Tested

Element	Percent Composition (wt%)			
	UNS S31603		UNS N08367	
	Specification	Actual	Specification	Actual
C	0.03 max.	0.026	0.030 max.	0.014
Cr	16.0-18.0	16.28	20.0-22.0	20.38
Ni	10.0-14.0	10.16	23.5-25.5	23.92
Mo	2.0-3.0	2.10	6.00-7.00	6.36
Cu	--	NR	--	0.13
N	--	0.040	0.18-0.25	0.230
Mn	2.00 max.	1.82	2.00 max.	0.24
Si	1.00 max.	0.44	1.00 max.	0.39
S	0.030 max.	0.001	0.030 max.	0.0005
P	0.045 max.	0.032	0.040 max.	0.019

NR = not reported in heat analysis

TABLE 2

Seawater Test Matrix

Test Code	Coating Cover and Conditions	Number of Specimens per Condition					
		S31603			N08367		
		3 Months	9 Months		3 Months	9 Months	
A	20% epoxy	3	3		3	3	
B	80% epoxy	3	3		3	3	
C	20% silane A	3	3		3	3	
D	80% silane A	3	3		3	3	
E	20% silane B	3	3		3	3	
F	80% silane B	3	3		3	3	
G	20% silane C	3	3		3	3	
H	80% silane C	3	3		3	3	
I	20% silane A + Cu	3	3		3	3	
H	80% silane A + Cu	3	3		3	3	
K	20% silane B + Cu	3	3		3	3	
L	80% silane B + Cu	3	3		3	3	
M	20% silane C + Cu	3	3		3	3	
N	80% silane C + Cu	3	3		3	3	
O	100% silane A + Cu	3	3		3	3	
P	100% silane B + Cu	3	3		3	3	
Q	100% silane C + Cu	3	3		3	3	
R	100% silane A + Cu + CP	3	3		3	3	
S	100% silane B + Cu + CP	3	3		3	3	
T	100% silane C + Cu + CP	3	3		3	3	

NOTES: All specimens O-T have scribed defects
Cu = ablative Cu type antifouling topcoat
CP = zinc anodes attached

TABLE 3

Source Seawater Hydrology
(Range of Results)

Parameter	Range of Data		9-Month Average
	Initial 3 Months	Full 9 Months	
Salinity ¹ (g/l)	33.77-37.29	31.34-37.74	34.15
Chlorinity ¹ (g/l)	18.61-20.64	17.73-20.89	19.19
Sulfate ² (mg/l)	2650-2790	2650-2790	2740
Dissolved O ₂ ¹ (mg/l)	4.52-7.73	4.52-9.33	6.76
pH ¹	7.8-8.2	7.8-8.2	8.0
Conductivity ² (mm hos/cm)	31.1-51.4	31.1-52.9	46.1
Sulfide ² (mg/l)	<0.005	<0.005	<0.005
Ammonia ² (mg/l)	<0.05	<0.05	<0.05
Total Iron ² (gm/l)	0.011-0.102	0.009-0.102	0.045
Copper ² (mg/l)	≤0.001	<0.001-0.005	0.002
Temperature ^{1,3} (°C)	17.9-27.4	9.0-27.4	18.8

¹ weekly analysis

² monthly analysis

³ sample temperature

TABLE 4

Summary of Seawater Temperatures (°C)

	Initial Three Months					Full Nine Months		
	Tank 1	Tank 2	Tank 3	Tank 4	Tank 5	Tank 3	Tank 4	Tank 5
MAX.	32.5	32.5	32.5	33.0	33.0	32.5	33.0	33.0
MIN.	22.0	22.5	18.0	20.0	22.0	18.0	20.0	18.0
AVG.	27.2	27.4	26.0	26.6	27.4	26.0	26.6	26.2
STD	2.1	2.1	2.7	2.6	2.1	2.7	2.6	2.7

TABLE 5

**Comparison of Corrosion Potential Range for Resistant and Attacked
Stainless Steels in 3 Month and 9 Month Filtered Seawater Tests**

Material	Coating	Potential Range (V) ¹	
		3 Months	9 Months
Resistant N08367	Epoxy + silane alone	+0.353 to +0.376	+0.452 to +0.472
Resistant N08367	Silane + Cu coated	+0.257 to +0.258	+0.281 to +0.309
Attacked S31603	All coatings	-0.157 to +0.119	-0.186 to +0.086
Attacked N08367	Epoxy	-0.030 to +0.104	-0.029 to +0.011
Copper ²	Bare metal	-0.375 to -0.300	
Zn Protected S31603 and N08367 ³	Silane + Cu coated	-0.975 to -0.925	-0.930 to -0.857
Zinc ²	Bare metal	-1.050 to -0.975	

¹ versus Ag/AgCl/Seawater reference

² approximate range given in "galvanic series" (ref. 14,15)

³ fully coated + scribed specimens

TABLE 6

**Summary of Crevice Corrosion Initiation Results for
Stainless Steel Controls Partially Coated with Epoxy**

Alloy and Percent Coating Coverage	Percent of Sites Attacked ¹		
	Current Testing		Earlier 6 Month Test
	3 Months	9 Months	
S31603 @ 20%	100	100	100
S31603 @ 80%	100	100	100
N08367 @ 20%	66.6	33.3	100
N08367 @ 80%	33.3	33.3	33.3

¹ based on 6 available sites/condition

TABLE 7

**Summary of Crevice Corrosion Propagation Results for Partially Coated with Epoxy
S31603 and N08367 Controls in 3-Month Seawater Tests**

Test Material	Affected Crevice Area (cm ²)					
	20% Coverage			80% Coverage		
	Panel No.	Code Side	Back	Panel No.	Code Side	Back
S31603	19	19.5	20.5	115	25.7	3.8
	20	21.5	23.4	116	3.4	28.7
	111	20.4	19.4	117	9.5	9.4
	Avg.	20.78		Avg.	13.42	
N08367	19	OK	OK	115	OK	OK
	20	2.0	19.3	116	0.1	15.2
	111	0.6	24.7	117	OK	OK
	Avg.	11.65		Avg.	7.65	

TABLE 8

**Summary of Crevice Corrosion Propagation Results for Partially Coated with Epoxy
S31603 and N08367 Controls in 9-Month Seawater Tests**

Test Material	Affected Crevice Area (cm ²)					
	20% Coverage			80% Coverage		
	Panel No.	Code Side	Back	Panel No.	Code Side	Back
S31603	112	33.5	39.0	118	33.2	36.0
	113	40.1	36.4	119	35.4	23.1
	114	35.0	36.9	120	38.0	35.0
	Avg.	36.82		Avg.	33.45	
N08367	112	0.8	6.2	118	1.0	2.6
	113	OK	OK	119	OK	OK
	114	OK	OK	120	OK	OK
	Avg.	3.5		Avg.	1.8	

TABLE 9

Summary of Crevice Corrosion Propagation Results for Epoxy Coated Controls

Alloy and Percent Coating Coverage	Mean Percent Affected Area ¹		
	Current Program		Earlier Program
	3-Month Test	9-Month Test	6-Month Test
S31603 @ 20% ²	33.6	59.4	67.0
S31603 @ 80% ³	4.8	12.0	9.9
N08367 @ 20%	18.8	5.7	12.3
N08367 @ 80%	2.8	0.6	0.2

¹ considers only attacked sites in mean value

² 20% coverage = 61.93 cm²/side

³ 80% coverage = 277.74 cm²/side

TABLE 10

**Crevice Corrosion Propagation Results for Epoxy Coated S31603
and N08367 Controls in 3-Month Seawater Tests**

Test Material	Maximum Depth of Attack (mm)					
	20% Paint Coverage			80% Paint Coverage		
	Panel No.	Code Side	Back	Panel No.	Code Side	Back
S31603	19	1.88	0.71	115	1.40	0.08
	20	1.40	1.14	116	1.55	0.10
	111	1.78	1.52	117	1.09	1.07
N08367	19	0.00	0.00	115	0.00	0.00
	20	0.20	0.46	116	<0.01	0.58
	111	0.64	0.89	117	0.00	0.00

TABLE 11

**Crevice Corrosion Propagation Results for Epoxy Coated S31603
and N08367 Controls in 9-Month Seawater Tests**

Test Material	Maximum Depth of Attack (mm)					
	20% Paint Coverage			80% paint Coverage		
	Panel No.	Code Side	Back	Panel No.	Code Side	Back
S31603	112*	0.59	1.94	118	0.80	1.08
	113*	1.88	1.95	119	1.44	1.28
	114*	1.98	0.68	120	1.29	1.03
N08367	112	0.44	1.20	118	0.10	0.29
	113	0.00	0.00	119	0.00	0.00
	114	0.00	0.00	120	0.00	0.00

* full thickness penetration at edge

TABLE 12

**Summary of Crevice Corrosion Propagation Results for
Stainless Steels Controls Partially Coated with Epoxy**

Alloy and Percent Coating Coverage	Maximum Depth of Attack (mm)*					
	Current Tests				Earlier Test	
	3 Months		9 Months		6 Months	
	Absolute Max.	Mean Max.	Absolute Max.	Mean Max.	Absolute Max.	Mean Max.
S31603 @ 20%	1.88	1.41	1.98	1.50	1.72	1.64
S31603 @ 80%	1.55	0.88	1.44	1.15	2.13	1.46
N08367 @ 20%	0.89	0.55	1.20	0.82	0.93	0.49
N08367 @ 80%	0.58	0.30	0.29	0.20	0.20	0.20

* excludes edge perforation for S31603 specimens

TABLE 13

Depth of Attack Results for S31603 Specimens Coated with Silane Alone

Coating and % Coverage	3-Month Test			9-Month Test		
	Panel	Code		Panel	Code	
	No.	Side	Back	No.	Side	Back
Silane A @ 20%	039	1.62	1.37	042	Perforated	
	040	Perforated		043	Perforated	
	041	1.72	2.08	044	Perforated	
Silane B @ 20%	051	0.31	1.96	054	Perforated	
	052	0.68	1.49	055	Perforated	
	053	2.02	1.27	056	Perforated	
Silane C @ 20%	063	2.19	1.43	066	Perforated	
	064	Perforated		067	Perforated	
	065	Perforated		068	Perforated	
Silane A @ 80%	045	0.97	0.12	048	Perforated	
	046	0.16	0.14	049	Perforated	
	047	0.22	0.76	050	Perforated	
Silane B @ 80%	057	0.87	1.38	060	Perforated	
	058	2.42	0.18	061	Perforated	
	059	1.57	1.84	062	Perforated	
Silane C @ 80%	069	0.34	2.04	072	1.12	1.04
	070	0.56	OK	073	1.65	OK
	071	0.61	1.47	074	1.54	2.03

TABLE 14

**Summary of Maximum Depth of Attack Incurred by
Stainless Steel Partially Coated with Silane Alone**

Alloy and Percent Coating Coverage	Depth of Attack (mm)					
	3-Month Test			9-Month Test		
	Max.	Mean		Max.	Mean	
	Depth	Value*	STD	Depth	Value*	STD
S31603						
Silane A @ 20%	Perf.	1.63	0.25	Perf.	>1.5	0.00
Silane B @ 20%	2.02	1.29	0.69	Perf.	>1.5	0.00
Silane C @ 20%	Perf.	1.60	0.29	Perf.	>1.5	0.00
S31603						
Silane A @ 80%	0.97	0.40	0.37	Perf.	>1.5	0.00
Silane B @ 80%	2.42	1.38	0.78	Perf.	>1.5	0.00
Silane C @ 80%	2.04	1.00	0.72	2.03	1.48	0.41
N08367						
Silane A @ 20%	Resistant			Resistant		
Silane B @ 20%	Resistant			Resistant		
Silane C @ 20%	Resistant			Resistant		
N08367						
Silane A @ 20%	Resistant			Resistant		
Silane B @ 20%	Resistant			Resistant		
Silane C @ 20%	Resistant			Resistant		

* Mean Value includes 1.50 mm data + ½ thickness of perforated sheet

TABLE 15

Depth of Attack Data for S31603 Specimens
Partially Coated with Silane + Ablative-Cu

	Maximum Depth of Attack with Coated Area (mm)					
	3-Month Test			9-Month Test		
	Panel No.	Code Side	Back	Panel No.	Code Side	Back
Silane A @ 20%	075	0.75	2.09	078	2.10	2.38
	076	2.11	1.87	079	1.95	2.11
	077	0.80	1.48	080	1.61	2.27
Silane B @ 20%	087	1.18	2.25	090	Perforated	
	088	1.80	2.23	091	Perforated	
	089	1.26	1.27	092	Perforated	
Silane C @ 20%	099	0.95	0.88	102	2.77	1.74
	100	1.47	1.78	103	Perforated	
	101	1.29	1.15	104	Perforated	
Silane A @ 80%	081	0.81	1.35	084	1.96	2.57
	082	0.47	0.52	085	Perforated	
	083	0.41	0.91	086	Perforated	
Silane B @ 80%	093	0.10	0.30	096	0.45	1.47
	094	0.48	0.87	097	1.82	2.07
	095	0.57	0.06	098	0.66	2.05
Silane C @ 80%	105	1.07	0.04	108	0.58	0.19
	106	0.05	0.17	109	1.34	0.24
	107	0.04	0.15	110	0.18	1.30

TABLE 16

Summary of Crevice Corrosion Propagation Results of Stainless Steels
Partially Coated with Silane + Ablative-Cu

Material And Coverage	Coated Area Affected							
	3-Month Test				9-Month Test			
	Max.		Mean	STD	Max.		Mean	STD
	(cm ²)	(%)	(%)	(%)	(cm ²)	(%)	(%)	(%)
S31603								
Silane A @ 20%	30	48	36.7	9.2	49	79	66.2	8.8
Silane B @ 20%	57	92	55.7	22.9	53	83	61.0	23.4
Silane C @ 20%	58	93	88.7	6.0	59	96	84.3	11.1
S31603								
Silane A @ 80%	27	11	6.3	2.9	25	10	6.0	2.2
Silane B @ 80%	25	10	5.9	2.7	15	6	4.5	2.0
Silane C @ 80%	69	28	15.8	8.5	156	63	21.5	22.0
N08367								
Silane A @ 20%	Resistant				Resistant			
Silane B @ 20%	Resistant				Resistant			
Silane C @ 20%	Resistant				Resistant			
N08367								
Silane A @ 80%	Resistant				Resistant			
Silane B @ 80%	Resistant				Resistant			
Silane C @ 80%	Resistant				Resistant			

TABLE 17

Percent Affected Area Data for S31603 Specimens
Partially Coated with Silane + Ablative-Cu

	Percent of Coated Area Attacked					
	3-Month Test			9-Month Test		
	Panel No.	Code Side	Back	Panel No.	Code Side	Back
Silane A @ 20% ¹	075	30	35	078	58	59
	076	35	47	079	70	79
	077	25	48	080	59	72
Silane B @ 20%	087	45	50	090	18	65
	088	35	37	091	56	85
	089	75	92	092	65	77
Silane C @ 20%	99	93	92	102	96	87
	100	82	92	103	70	72
	101	93	80	104	95	86
Silane A @ 80% ²	081	11	4	084	5	4
	082	4	8	085	5	10
	083	7	4	086	5	7
Silane B @ 80%	093	3	6	096	6	5
	094	10	5	097	6	2
	095	7	3	098	6	2
Silane C @ 80%	105	25	10	108	63	2
	106	28	8	109	8	20
	107	12	12	110	11	25

¹ 20% = 62 cm²/side

² 80% = 248 cm²/side

TABLE 18

Crevice Corrosion Propagation Results for Stainless Steels
Partially Coated with Silane + Ablative-Cu

Alloy and Percent Coating Coverage	Summary of Maximum Depth of Attack (mm)					
	3-Month Test			9-Month Test		
	Absolute Max.	Mean Max.	Standard Deviation	Absolute Max.	Mean Max.	Standard Deviation
S31603						
Silane A @ 20%	2.11	1.52	0.62	2.38	2.07	0.27
Silane B @ 20%	2.25	1.67	0.50	Perforated	1.50	0.00
Silane C @ 20%	1.78	1.25	0.34	Perforated	1.75	0.51
S31603						
Silane A @ 80%	1.35	0.75	0.36	Perforated	1.76	0.44
Silane B @ 80%	0.87	0.40	0.31	1.82	1.42	0.71
Silane C @ 80%	1.07	0.25	0.40	1.34	0.63	0.55
N08367						
Silane A @ 20%	Resistant			Resistant		
Silane B @ 20%	Resistant			Resistant		
Silane C @ 20%	Resistant			Resistant		
N08367						
Silane A @ 80%	Resistant			Resistant		
Silane B @ 80%	Resistant			Resistant		
Silane C @ 80%	Resistant			Resistant		

TABLE 19

**Summary of Propagation Results for Fully Coated + Scribed
Stainless Steel Specimens**

Alloy and Coating	Affected Area Data					
	3-Month Test			9-Month Test		
	Maximum		Mean	Maximum		Mean
	(cm ²)	(%)	(%)	(cm ²)	(%)	(%)
S31603						
Silane A	~9	3	1.8	~6	2	1.5
Silane B	~9	3	1.8	~9	3	1.3
Silane B	~9	3	1.8	~9	3	1.5
N08367						
Silane A	Resistant			Resistant		
Silane B	Resistant			Resistant		
Silane C	Resistant			Resistant		

TABLE 20

**Summary of Depth of Attack Results for Fully Coated + Scribed
Stainless Steel Specimens**

Alloy and Coating	Maximum Depth of Attack Data			
	3-Month Test		9-Month Test	
	Max.(mm)	Mean (mm)	Max. (mm)	Mean (mm)
S31603				
Silane A	0.22	0.10	2.28	0.86
Silane B	0.09	0.06	1.38	0.32
Silane C	0.07	0.06	0.20	0.11
N08367				
Silane A	Resistant		Resistant	
Silane B	Resistant		Resistant	
Silane C	Resistant		Resistant	

APPENDIX 1

Copy of Revised NACE CORROSION/2002 Paper No. 02187
With Color Reproduced Photographs

SEAWATER CREVICE CORROSION RESISTANCE OF STAINLESS STEELS COATED WITH SILANE AND ANTIFOULING PAINT SYSTEMS

R. M. Kain
LaQue Center for Corrosion Technology, Inc.
P. O. Box 656
Wrightsville Beach, NC 28480

ABSTRACT

Interest in the use of non-magnetic stainless steels for ship hull construction has focused attention on candidate coating systems with antifouling resistance. This attention is elevated by the knowledge that subject austenitic grades are not inherently fouling resistant, and, in some cases, may be prone to localized corrosion at marine attachment, e.g., barnacles, sites. Moreover, it has already been demonstrated that coating of candidate austenitic alloys with epoxy and epoxy + antifouling paint systems can promote crevice corrosion at coating-to-bare metal interfaces, especially when the surface area of the latter becomes large. Various investigations are underway by different researchers to identify a compatible coating system to minimize fouling without creating adverse conditions for crevice corrosion. This paper describes a nine-month seawater test program involving exposure of 240 stainless steel test specimens, mostly treated with water-base and solvent-base silane and topcoated with ablative Cu antifouling paint.

Interim, three-month, test results presented indicate marked improvement in localized corrosion resistance for silane treated "20Cr-6Mo" stainless steel (UNS N08367) over that exhibited by test specimens coated with epoxy alone. These same benefits were not observed when the silane treatments, formulated for the N08367 alloy, were applied to UNS S31603.

Keywords: austenitic stainless steels, crevice corrosion, seawater, silane, antifouling paint

INTRODUCTION

While austenitic stainless steels have many attributes, their lack of inherent fouling resistance and the propensity for some grades to suffer crevice corrosion demand attention when designing for certain seawater applications. The potential use of austenitic stainless steels for ship hull applications, for example, has generated interest in investigating the influence of coatings on the fouling and crevice corrosion resistance of select grades including S31603, S20910 and N08367.¹⁻⁴

In the absence of antifouling protection, localized corrosion associated with barnacle growth can affect the 300 series alloys and others.^{5,6} As a general guide, those stainlesses with less than 6 percent molybdenum are the most likely to be attacked.⁷ While antifouling coatings can prevent or largely limit attachment by barnacle and other macrofoulers, coatings may serve as crevice formers in their own right. Previous work, for example, has shown that the above mentioned grades can be susceptible to crevice corrosion at coating to bare metal sites.^{2,3} As reported, epoxy coated stainless steel and epoxy + antifouling top coated stainless steel were significantly affected when tested with large areas of bare metal, e.g., 20% and 80%. In contrast, fully coated test panels with intentionally scribed defects exhibited comparatively little attack in tests lasting up to one year.

As recently described by Sedriks¹, the use of a zinc-rich primer paint beneath the initial coat of epoxy cover has been employed to mitigate the chances for crevice corrosion at scratches and larger damage sites. One concern about the use of zinc-rich primer is the potential for liquid metal embrittlement of the stainless steel should the need for repair welding or high temperature cutting arise.^{1,8-10} Because of this added consideration, alternative coating systems to replace the zinc primer are being investigated.¹ Those covered in the present report are based on experimental organic silane formulations comprising 1:5 mixtures of vinyltriacetoxysilane (VTAS) and bis-amino silane.^{11,12} Existing antifouling paints of the ablative copper (Cu) and high surface energy elastomeric types are traditionally used in conjunction with epoxy undercoats.^{1,2} On steel hull vessels, the epoxy serves as a corrosion barrier coating. Ideally, the subject silane coatings would eliminate the need for both the zinc-rich primer, and the epoxy barrier coating when applying antifouling paint to stainless steel. Some reported advantages of silanes include: environmental friendliness, process control, excellent adhesion between metals and other paint, ultra-thin films and anticorrosion performance.^{11,12}

It is the intent of this paper to document the preparation of 240 stainless steel test specimens and to provide interim three-month test results for work in progress. Final evaluation results for a replicate series of test specimens scheduled for nine months exposure will be presented in a subsequent paper.

EXPERIMENTAL

Materials and Specimens

Present testing comprised UNS S31603 and N08367 stainless steels having the chemical compositions listed in Table 1. For comparison, the compositions of previously tested material² are also included. Table 2 provides equivalent $\text{Cr} + 3.3 \times \text{Mo} + 16 \times \text{N}$ values for the respective materials. For both materials, the equivalents for both heats are nearly identical. These actual values are somewhat lower than those based on the respective nominal compositions cited by Sedriks.¹

A total of 120 specimens measuring 100 mm x 300 mm (4-inch x 12-inch) were laser cut from nominally 3 mm (0.125-inch) thick sheet stock of each of the respective materials. Additional preparation included edge grinding and rounding, and the drilling of a 13 mm (1/2-inch) support hole at

one corner. An additional 13 mm hole was drilled for subsequent attachment of zinc anodes to 18 specimens of each material. Both surfaces and all edges were then grit blasted with fresh 80 mesh Al oxide to create an anchor profile for eventual coating application. For the 2B mill provided S31603 sheet, the resulting surface roughness after grit blasting was approximately $3.0\text{ }\mu\text{m}$ ($120\text{ }\mu\text{in}$), and that for the N08367 was $2.8\text{ }\mu\text{m}$ ($110\text{ }\mu\text{in}$). Both the present and previously tested N08367 sheet material initially had rougher surfaces than the as-provided 2B mill finish on the S31603.

Coatings and Application

In preparation for coating, all grit blasted specimens were subjected to a degreasing rinse with acetone. Specimens scheduled for silane coating were dipped in a hot ($60\text{--}70^{\circ}\text{C}$) 7.5% commercial alkaline bath for 3-5 minutes and air-dried. Using professional quality masking tape, 42 specimens of each material were masked to allow eventual coating over 20 percent of both surfaces. Another 42 specimens were thusly prepared for 80 percent coverage.

Twelve specimens, six at 20 percent and six at 80 percent, were subsequently coated with epoxy, silane or silane + ablative Cu systems as indicated in Table 3. The epoxy system was the same 2-coat (gray over red), 2-part barrier type paint used in the previously referenced investigation.² Whereas the earlier test specimens were spray coated, those in the present test program were brushed. The combined dry film thickness of the two-layer epoxy coating was approximately 250 to 300 μm ($\sim 10\text{--}12$ mils).

Three experimental silane coatings identified in Table 4 were prepared and applied by researchers at the University of Cincinnati. All three were formulated for use with N08367 and intended to be top-coated with the selected rosin based ablative Cu antifouling paint. The same formulations were applied to the present S31603 specimens without any prequalification. Those fully coated were dipped, while those which received only 20 or 80 percent coverage were brushed with silane. Reportedly, the dry film thickness of the silane coatings is $<1\text{ }\mu\text{m}$. The ablative Cu paint was also the same used in the previous investigation², but brush applied at the test site. The combined silane + ablative Cu coating thickness was approximately the same as that for the above epoxy system.

In addition to the partially coated specimens identified in Table 3, specimens of each material were fully coated with each of the silane formulations and fully topcoated with the ablative Cu. Both sides of each fully coated specimen received a 203 mm (8-inch) long scribe to expose the substrate stainless steel. A carbide tipped lathe tool was used to score the paint layers. Figure 1 (a-c) provides a schematic representation of the various specimen types.

Zinc Anode Application

Thirty-six of the fully coated specimens identified in Table 3 were selected for testing with zinc anodes. As in the previous investigation, additional preparation comprised use of a counter bore to remove the paint, and some surface metal, at the intended attachment site. Subsequently, two zinc anodes (Mil. Spec. A-18001), each 25.4 mm in diameter x 25.4 mm long (1-inch x 1-inch) were attached and secured with an "18-8" stainless steel ($1/4\text{--}20$) fastener, see Figure 1d.

Exposure Conditions

Five 400-liter (~ 105 gal) seawater test tanks, each equipped with recirculation pumps, auxiliary quartz heaters and controllers were prepared (Figure 2). Four tanks were designated for freely corroding

specimens. Two tanks were designed for testing of triplicate specimens for three months and two others for triplicates exposed for nine months. Separate tanks were utilized for those specimens coated with ablative Cu antifouling paint. The fifth tank contained all those fitted with zinc anodes.

Fresh filtered (5-10 μm) natural seawater at the LaQue Center for Corrosion Technology, Inc.'s Wrightsville Beach, NC, test site was continuously supplied to each tank at a rate of approximately 1.9 l/m (0.5 gpm). Typical seawater characteristics are shown in Table 5. Ambient seawater temperature at test initiation was 27°C. The average daily temperature in each of the five tanks during the initial three-month exposure ranged from 27.2°C to 27.8°C (Std. Dev. 2.1°C). An auxiliary heating system provided temperature control within a target range of 25°C \pm 5°C.

Interim Inspections

Specimens were routinely inspected in-situ during the initial three months of testing in order to detect the on-set of any attack. The results from these in-situ inspections contribute to this interim paper.

Three-Month Removal Procedure

Immediately prior to removal, the corrosion potential of the partially coated specimens and those fully coated ones protected with zinc anodes were measured with the aid of an alloy N06625 pointed probe, a Ag/AgCl/Seawater reference electrode and a high impedance digital voltmeter.

After removal, each of the 120 specimens (identified in Table 3) were brushed to remove loose corrosion product and, in some cases, disbonded coating. A dental pic was used to further remove loose epoxy at sites where crevice corrosion occurred. All specimens without the ablative Cu topcoat were briefly dipped in 30% nitric acid (room temperature) to remove calcareous deposits from the base metal surfaces. For the partially coated specimens with the ablative Cu, only the bare metal portion was cleaned with nitric-acid, by brushing. All freely corroding specimens were rebrushed with detergent, rinsed and dried in preparation for final inspection. As reported herein, affected crevice area was quantified with a transparent grid and depths of attack measured with a needlepoint dial depth gauge.

One cathodically protected specimen was selected at random and dipped in 10% sulfuric acid (room temperature) to remove calcareous deposits which formed on the ablative Cu coating and at the scribed area.

TEST RESULTS AND DISCUSSION

In-Situ Inspection Results

In-situ inspections performed during the initial three months of testing revealed information concerning localized corrosion at the primary coating-to-bare metal interface sites, and elsewhere. The following summarizes the initial behavior of all specimens, including those in the ongoing nine-month test.

Epoxy Coated Controls. Visual evidence of attack was detected at 17 of the available 24 primary sites on the epoxy coated S31603 specimens within three days. Four additional sites were recorded within nine days, and the remaining three within 21 days. In contrast, similar attack of epoxy coated

N08367 specimens during the initial three months was limited to five sites total. Times for visual detection ranged from 21 to 42 days.

Silane Alone. All thirty-six N08367 specimens that were partially coated with silane A, B and C appeared to be fully resistant during the initial three-month period. In contrast, all of the corresponding S31603 specimens exhibited the on-set of attack at bare and/or coated surface sites within six days; edges were particularly affected. In contrast to the previously discussed epoxy coated specimens, those with 20% and 80% silane coverage showed little or no attack at the primary interface sites.

Silane + Ablative Cu (partially coated). No evidence of attack at the primary interface sites, or elsewhere, was detected for any of the thirty-six N08367 specimens top coated with ablative Cu antifouling paint.

Several of the silane + Cu top coated S31603 specimens exhibited crevice attack at the primary interface sites within three days. By day 60, a total of 22 of the available 72 primary sites showed some degree of attack. These were largely on those specimens with the silane B and C treatments. In addition to the above, all S31603 specimens in this group exhibited attack on a bare and/or coated surface.

Silane + Ablative Cu (fully coated). All 18 of the fully coated + scribed N08367 specimens appeared to be resistant to attack at the intentional defect sites and elsewhere during the initial three months of testing. In contrast, 11 of the 36 scribed sites on the corresponding S31603 specimens exhibited attack at these designated locations. The earliest detection time, as noted on one specimen bearing each of the three silane coatings, was three days. All 18 fully coated S31603 specimens exhibited some attack at the scribe or elsewhere within 42 days. In contrast to the partially coated specimens with larger cathodic bare metal areas, the volume of corrosion product generated on the fully coating + scribed specimens was considerably less.

Cathodically Protected Specimens. No evidence of substrate corrosion was detected in-situ on any of the fully coated (silane + ablative Cu) S31603 and N08367 specimens with zinc anode protection. However, changes in the appearance of ablative Cu were detected within a few days, and progressed through the initial days of exposure. These changes initially appeared as narrow gray-black streaks, which later broadened and coalesced into larger areas. Such behavior was not previously observed after one full year exposure of epoxy + ablative Cu coated specimens cited in reference 2.

Final Evaluation of Freely Corroding Specimens

N08367 Results. Final inspection of the sixty N08367 specimens removed after three months exposure confirmed the in-situ observations indicated above. While all silane (A, B, and C) and silane + ablative Cu coated specimens were found to be completely resistant to pitting and crevice corrosion, three of the six specimens partially coated with epoxy were attacked. Figure 3 provides a representative view of an affected epoxy coated specimen and correspondingly resistant silane and silane + ablative Cu coated specimens (all 20% coverage). As indicated in Table 6, crevice corrosion affected a total of six sites, including one minimally. As summarized in Table 7, crevice corrosion propagation incurred in the present three-month test approximated that reported for the earlier six-month test.²

S31603 Results. Again, these final inspection results confirmed the in-situ observations. As shown in Table 6, all sites on the presently removed epoxy coated specimens exhibited crevice corrosion. While the affected area data, summarized in Table 7, was about one-half that incurred in the earlier six-month test², the maximum depth of attack data more closely approximate the longer term data,

especially for those specimens with the greater surface area of exposed metal. As shown, for example, in Figure 4, some bare metal surface pitting was also confirmed.

In contrast to the above, S31603 specimens partially coated with silane treatments A, B, and C exhibited extensive pitting in coated and non-coated areas, including the edges, but no crevice attack per se. In the absence of any extensive crevice corrosion, initiated pits propagated with the assist of gravity (Figure 5).

All S31603 specimens with 20% of the surfaces coated with silane + ablative Cu exhibited crevice-like attack. However, in contrast to the epoxy coated controls, the attack appeared to propagate inward from the edges and other initiation sites rather than from the primary interface with the bare metal. As shown by Figure 6, some influence of silane formulation on the overall extent of attack is apparent from the visual ranking $A < B < C$. Except for attack at apparent pit initiation sites, the attack beneath the silane + ablative Cu was relatively light, as contrasted with that found beneath the epoxy.

Overall, S31603 specimens with 80% of the surface coated with silane + ablative Cu exhibited less attack, both pitting and crevice related, than did those with 20% coverage. While those with the silane C treatment again appeared to be the most affected, the difference between A and B treated material was less distinguishable.

For the fully coated + scribed S31603, some attack was found at the scribed area and/or elsewhere regardless of silane formulation. Examples are provided in Figure 7. After cleaning inspection revealed only superficial penetration. The morphology of the attack on this group of coated S31603 specimens is reminiscent of filiform type attack. At this stage of the evaluation process, quantification of pit depths and the extent of under coating damage, other than for the epoxy coated specimens had not been attempted.

Cathodically Protected Specimens

Post three-month test inspection of the 18 cathodically protected S31603 and N08367 specimens listed in Table 3 revealed that the previously observed streaking and discoloration was actually related to the formation of calcareous deposits on the ablative Cu surface and within the scribed areas. This implies that the very thin silane precoat layer did not provide an effective insulating barrier in the manner associated with the use of epoxy beneath the anti fouling paint. The extent of calcareous deposition appears to follow the visual ranking silane $A < B < C$. In addition, exposure under these conditions promoted coating disbondment, vis-a-vis blistering. To a lesser extent, blistering was also detected in the previously reference one-year test for S31603, S20910 and N08367 where epoxy was applied prior to top coating with ablative Cu or elastomeric antifouling paints.

Corrosion Potential Data

Table 8 provides a summary of the corrosion potentials obtained for the indicated groups of specimens at the conclusion of the three-month test period. Data has been arranged as a "galvanic series" with the resistant N08367 epoxy and silane coated specimens at the noble (more electro-positive) end of the scale, and the cathodically protected specimens at the active (more electro-negative) end. Also indicated are the potentials for copper metal and zinc from previously published "galvanic series" in seawater.¹³ In the absence of a suitable base metal contact point, no measurements were attempted for the fully coated + scribed specimens tested under freely corroding conditions. For the resistant

N08367 specimens, i.e., those without ablative Cu, the ennobled potentials can be attributed the metal's inherent passive film, biofilm formation¹⁴ and the absence of any active crevice attack.

For all other specimens listed in Table 8, the values shown represent some mixed-potential arising from the following galvanic situations: resistant (exposed) and active crevice/pitted areas, substrate metal and Cu coating, or the preceding and the Zn anodes. As can be seen, the potentials for the resistant N08367 specimens with silane + ablative Cu are about 0.100V less noble than the corresponding specimens with epoxy or silane alone. It is presently unknown if this shift in potential is due entirely to the galvanic influence of the more active copper, or perhaps with some additional influence of the copper presence on the biofilm ennoblement process on the bare metal.

The data in Table 8 shows that the potential for the cathodically protected specimens approached that for zinc. Within this potential domain, the antifouling characteristics of the ablative Cu coating would expectedly be negated. In the previous test², the presence of the insulating epoxy barrier coat prevented the antifouling topcoat from being influenced by the Zn anodes.

SUMMARY AND CONCLUSIONS

The preparation and testing of 240 stainless steel specimens with various coatings has been described. This work, and that of others, is aimed at identifying an effective coating system that will prevent marine fouling on austenitic stainless steels without making the substrate material prone to crevice corrosion. The present investigation has focused on the use of silane coatings formulated for use with the "20 Cr-6Mo" alloy UNS N08367 and top coated with a rosin base, ablative Cu antifouling paint. Testing also comprised UNS S31603 and the application of epoxy paint on control specimens.

Based on the removal and evaluation of 120 coated test specimens exposed to warm seawater for three months, silane formulated especially for use with N08367 and the selected ablative Cu coating appears to hold promise. Its effectiveness will be further assessed following subsequent evaluation of a like number of replicate specimens being tested for a full nine months. Presently, the silane coatings that were formulated for use with N08367 have not been effective for use with the more crevice prone grade S31603. Supporting observation and conclusions are as follows:

- In terms of crevice corrosion initiation, the performance of S31603 and N08367 specimen controls with partial epoxy coverage followed the trends established in earlier tests.²
- In the case of all other freely corroding specimens, those of the 20Cr-6Mo alloy, N08367, are clearly more resistant than the S31603 material. Except for those with the epoxy coating, no other N08367 specimens were attacked during the initial three months of seawater testing.
- Regarding specimens coated only with silane, S31603 exhibited severe attack at bare and coated edges and elsewhere.
- Topcoating of the S31603 specimens with ablative Cu (over silane) appears to result in more attack within the coated region; the extent of which is apparently affording some protection to otherwise susceptible bare areas (i.e., edges). Test panels precoated with silane C exhibited more coating related attack than those precoated with silane A or silane B, respectively.

- Some attack has been observed at intentional scribe sites and elsewhere on fully coated S31603 specimens. Due to the limited amount of bare (cathodic) surface area, this attack is minimal in comparison to that for specimens tested with 20% and 80% bare surface exposed.
- Zinc anodes provided corrosion protection to the substrate stainless steels. However, due to the ultra thin nature of the silane film, it is apparent that the ablative Cu was also being polarized. This was evidenced by the development of calcareous deposits on the topcoat. Cathodic protection also resulted in significantly more coating disbondment and blistering on the silane treated specimens than was observed previously when epoxy coating preceded the antifouling coating.
- Following the removal of triplicate specimens for each alloy-coating condition after nine months exposure, additional information on localized corrosion initiation and propagation will be presented in a subsequent paper.

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TABLE 1
CHEMICAL ANALYSIS OF CURRENT AND PREVIOUSLY TESTED STAINLESS STEELS

	C	Cr	Ni	Mo	Cu	N	Mn	Si	S	P
N08367										
Current heat	0.014	20.38	23.92	6.25	0.13	0.230	0.24	0.39	0.0005	0.019
Ref. #2 heat	0.017	20.45	23.90	6.22	0.21	0.210	0.35	0.39	0.0004	0.021
S31603										
Current heat	0.026	16.28	10.16	2.10	NR	0.040	1.82	0.44	0.001	0.032
Ref. #2 (heat 2)	0.010	16.42	10.23	2.10	--	0.04	1.89	0.48	0.001	0.028

TABLE 2
Cr + 3.30 Mo + 16 N Equivalents

Material	Current Heat	Ref. #2
N08367	44.69	44.34
S31603	23.85	23.99 (heat 2)

TABLE 3
SEAWATER TEST MATRIX

Test Code	Coating Cover and Conditions	Number of Specimens per Condition			
		S31603		N08367	
		3 Months	9 Months	3 Months	9 Months
A	20% epoxy	3	3	3	3
B	80% epoxy	3	3	3	3
C	20% silane A	3	3	3	3
D	80% silane A	3	3	3	3
E	20% silane B	3	3	3	3
F	80% silane B	3	3	3	3
G	20% silane C	3	3	3	3
H	80% silane C	3	3	3	3
I	20% silane A + Cu	3	3	3	3
H	80% silane A + Cu	3	3	3	3
K	20% silane B + Cu	3	3	3	3
L	80% silane B + Cu	3	3	3	3
M	20% silane C + Cu	3	3	3	3
N	80% silane C + Cu	3	3	3	3
O	100% silane A + Cu	3	3	3	3
P	100% silane B + Cu	3	3	3	3
Q	100% silane C + Cu	3	3	3	3
R	100% silane A + Cu + CP	3	3	3	3
S	100% silane B + Cu + CP	3	3	3	3
T	100% silane C + Cu + CP	3	3	3	3

NOTES: All specimens O-T have scribed defects
 Cu = ablative Cu type antifouling topcoat
 CP = zinc anodes attached

TABLE 4
Generic Description of Tested Silane Coatings (by volume)

Silane A	2% silane + 98% DI water base
Silane B	2% silane + 98% DI water base
Silane C	2% silane + 2% DI water + 96% ethanol

TABLE 5
SEAWATER HYDROLOGY*

Salinity	32.76 to 35.04 g/l
Chlorinity	18.22 to 19.39 g/L
Sulfate	2345 to 2732 mg/l
Dissolved O ₂	6.57 to 7.30 mg/L
pH	7.9 to 8.0
Conductivity	42.1 to 53.1 mmhos/cm
Sulfide	<0.005 mg/l
Ammonia	<0.05 mg/l
Total Fe	0.083 to 0.134 mg/l
Copper	0.001 to 0.004 mg/l
Temperature	17.6° to 20.4°C

*most recent 10-year average results

TABLE 6
CREVICE CORROSION INITIATION AND PROPAGATION BEHAVIOR
FOR EPOXY COATED S31606 AND N08367 CONTROLS
IN THREE-MONTH FILTERED SEAWATER TEST

Test Material	Affected Crevice Area (cm ²)					
	20% Paint Coverage			80% Paint Coverage		
	Panel No.	Code Side	Back	Panel No.	Code Side	Back
S31603	19	19.5	20.5	115	25.7	3.8
	20	21.5	23.4	116	3.4	28.7
	111	20.4	19.4	117	9.5	9.4
N08367	19	OK	OK	115	OK	OK
	20	2.0	19.3	116	0.1	15.2
	111	0.6	24.7	117	OK	OK

OK = no visible attack

Test Material	Maximum Depth of Attack (mm) ¹					
	20% Paint Coverage			80% Paint Coverage		
	Panel No.	Code Side	Back	Panel No.	Code Side	Back
S31603	19	1.88	0.71	115	1.40	0.08
	20	1.40	1.14	116	1.55	0.10
	111	1.78	1.52	117	1.09	1.07
N08367	19	0.00	0.00	115	0.00	0.00
	20	0.20	0.46	116	<0.01	0.58
	111	0.64	0.89	117	0.00	0.00

¹ Excludes perforated edges on S31603 specimens

TABLE 7
COMPARISON OF PRESENT THREE-MONTH AND EARLIER SIX-MONTH
TEST RESULTS FOR EPOXY COATED CONTROLS

Alloy and % Coating Coverage	Three-Month Exposure			Six Month Exposure ¹		
	% of Sites Attacked (6 max.)	Affected Area - Avg. (cm ²)	Maximum Depth (mm)	% of Sites Attacked (3 max.) ¹	Affected Area - Avg. (cm ²)	Maximum Depth (mm)
S31603 @ 20%	100	20.8	1.88	100	41.5	1.72
S31603 @ 80%	100	13.4	1.55	100	27.4	2.13
N08367 @ 20%	66.6	11.7	0.89	100	7.6	0.93
N08367 @ 80%	33.3	7.6	0.58	33.3	0.6	0.20

¹ Ref. 2 exposures included grit blasted and mill produced surfaces. Data shown is for grit blasted only.

TABLE 8
CORROSION POTENTIALS FOR
VARIOUS COATED TEST SPECIMENS AND OTHER METALS

Material (coating)	Potential Range (V) ¹ (Noble to Active Ranking)
Resistant N08367 (epoxy and silane)	+0.353 to +0.376
Resistant N08367 (silane + ablative Cu)	+0.257 to +0.278
Corroded S31603 (all coatings)	-0.157 to +0.119
Corroded N08367 (epoxy)	-0.030 to +0.104
Copper ² (bare metal)	-0.375 to -0.300
Zinc protected S31603 and N08367 (silane + ablative Cu) ³	-0.975 to -0.925
Zinc ² (bare metal)	-1.05 to -0.975

¹ vs. Ag/AgCl/Seawater reference

² Published "galvanic series"¹³ (approximate range)

³ Fully coated + scribed specimens, all others listed were partially coated.

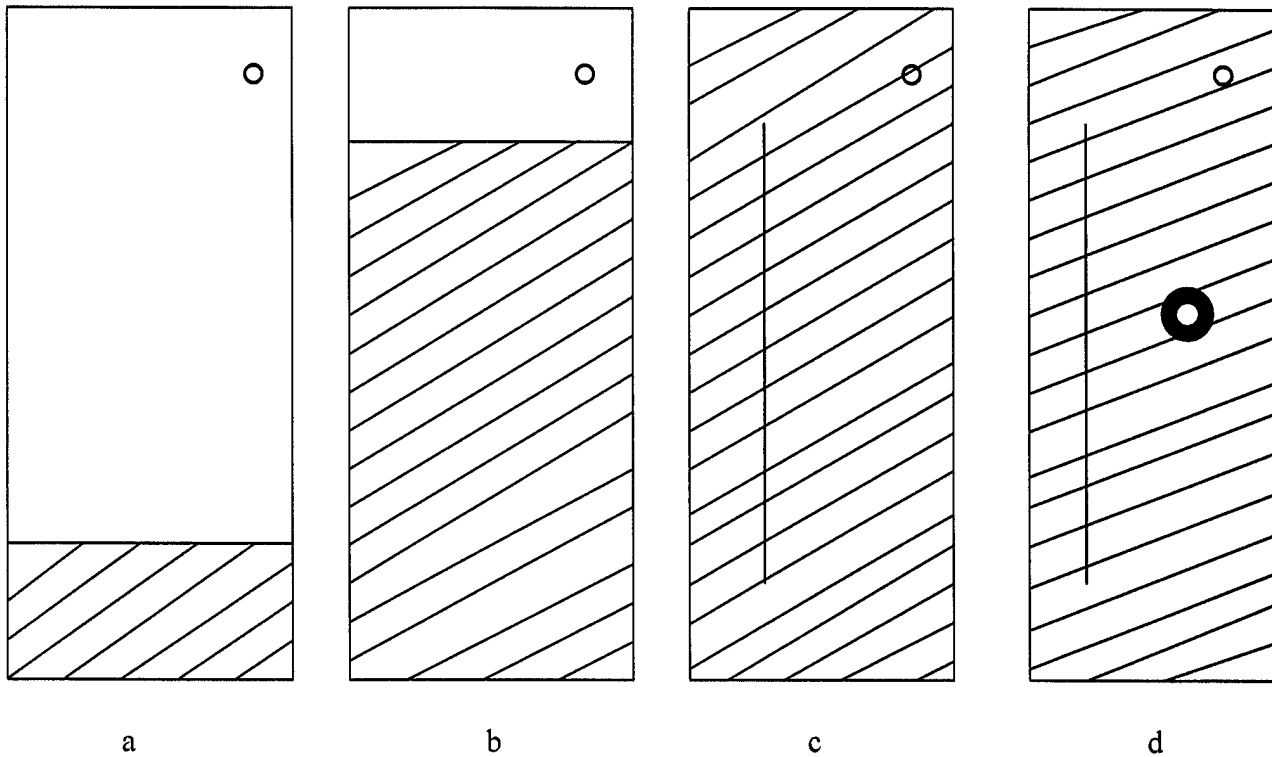


FIGURE 1- Schematic representation of various coated specimens tested.
a – 20% coverage with epoxy, or silane, or silane + ablative Cu
b – 80% coverage as for Type a
c – 100% coverage with silane + ablative Cu and scribed
d – 100% coverage as for Type c with Zn anodes attached

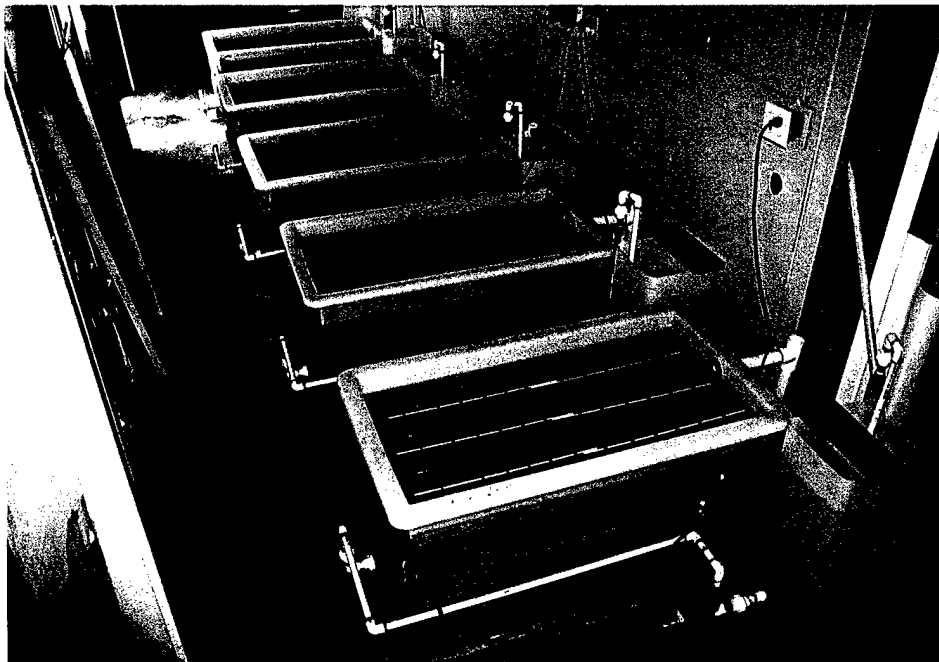


FIGURE 2 – Overall view of five-tank test station for evaluating coated stainless steel in seawater.

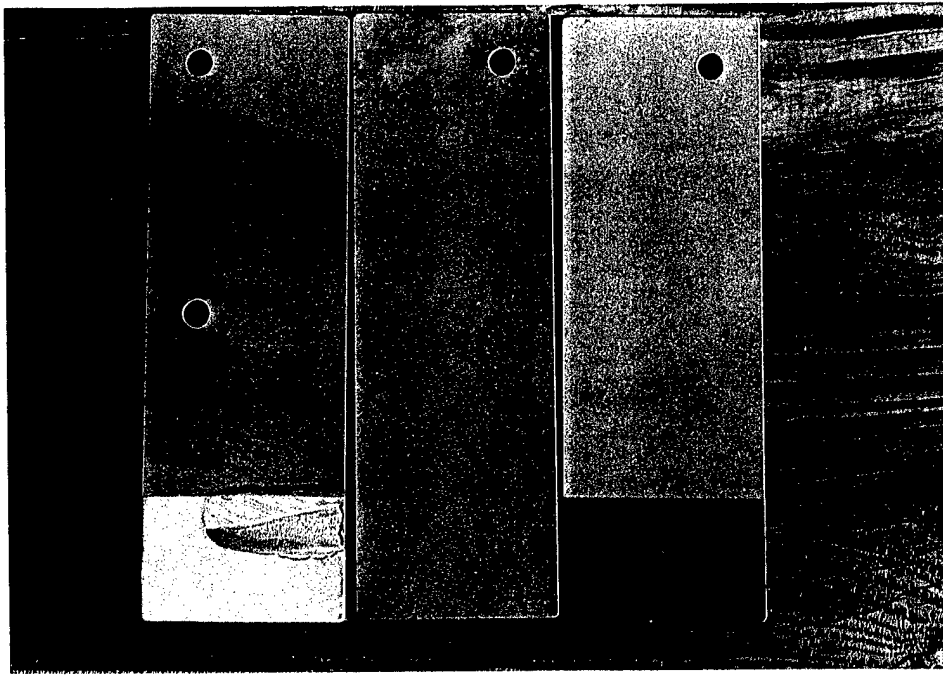


FIGURE 3 – Representative view (left) affected epoxy coated and (center and right) resistant silane and silane + ablative Cu coated N08367 specimens after three months seawater exposure.

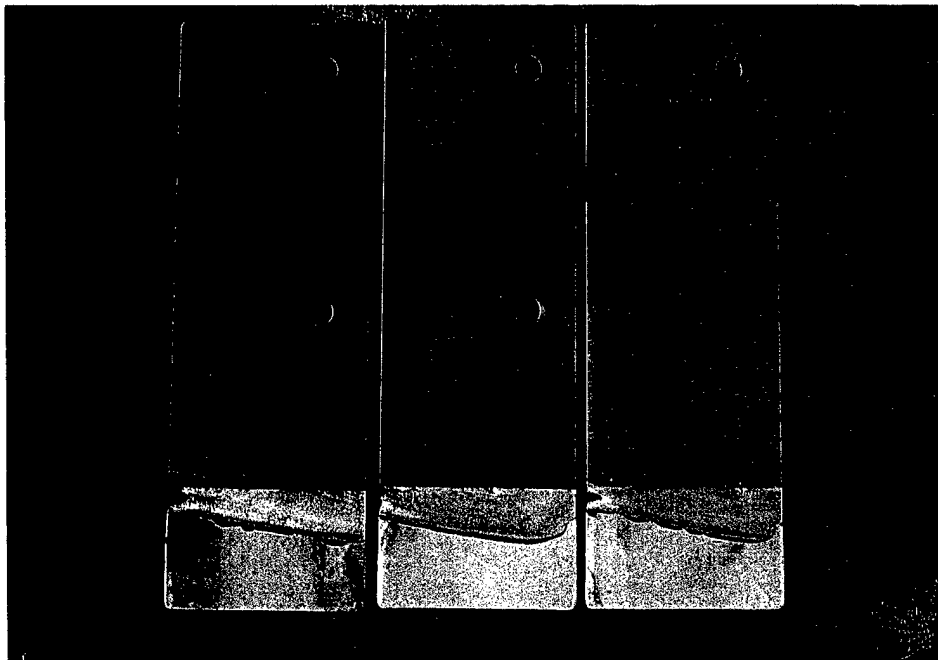


FIGURE 4 – View of partially cleaned S31603 specimens with 20% epoxy coverage showing extensive crevice corrosion and pitting.

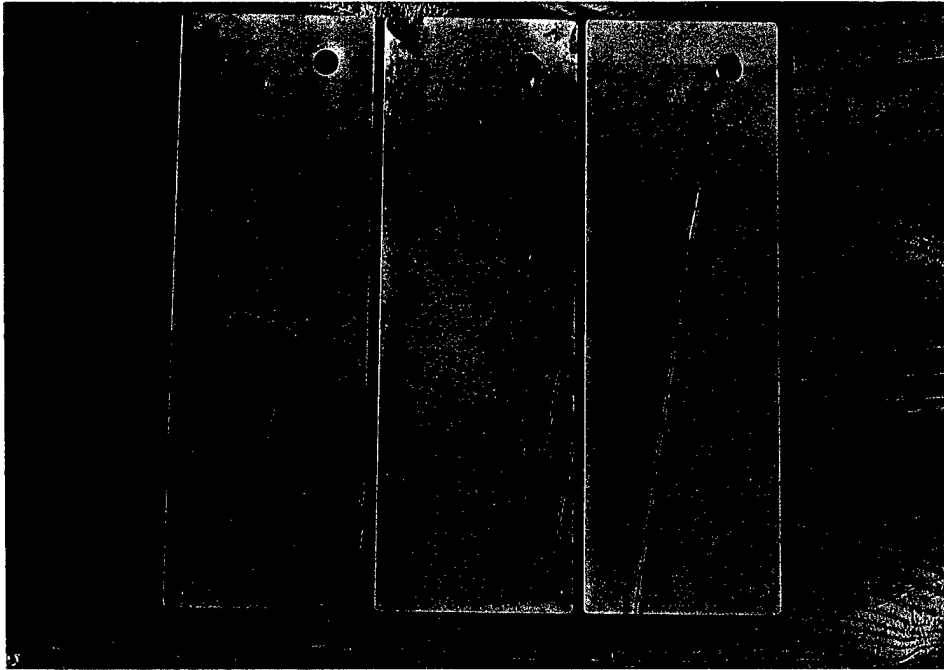


FIGURE 5 – View of partially cleaned S31603 specimens with 80% silane coverage (left to right: Silane A, B and C).

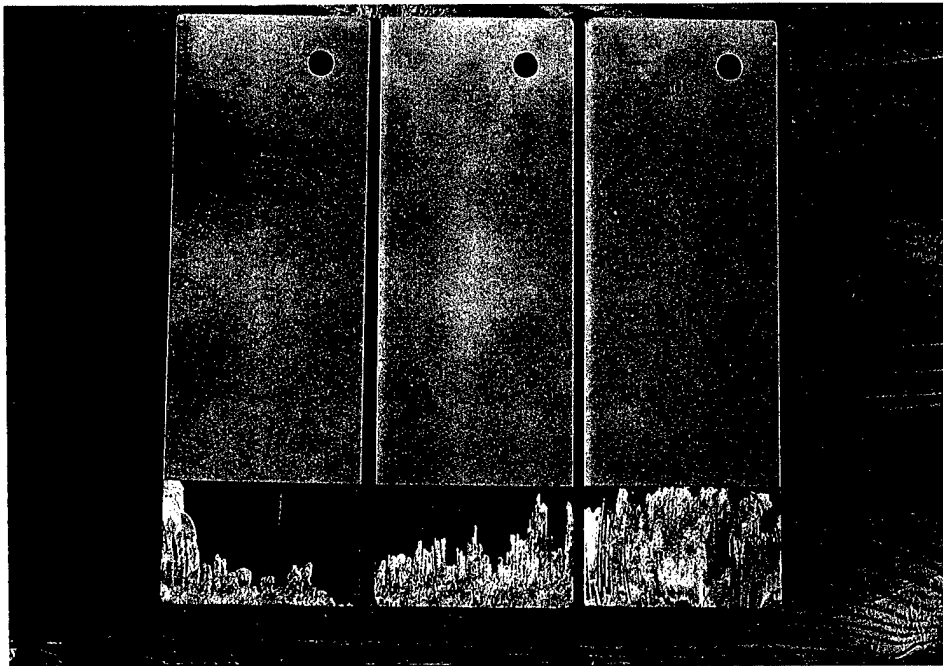


FIGURE 6 – After-cleaning view of S31603 specimens with 20% silane + ablative Cu (left to right: Silane A, B and C precoated)

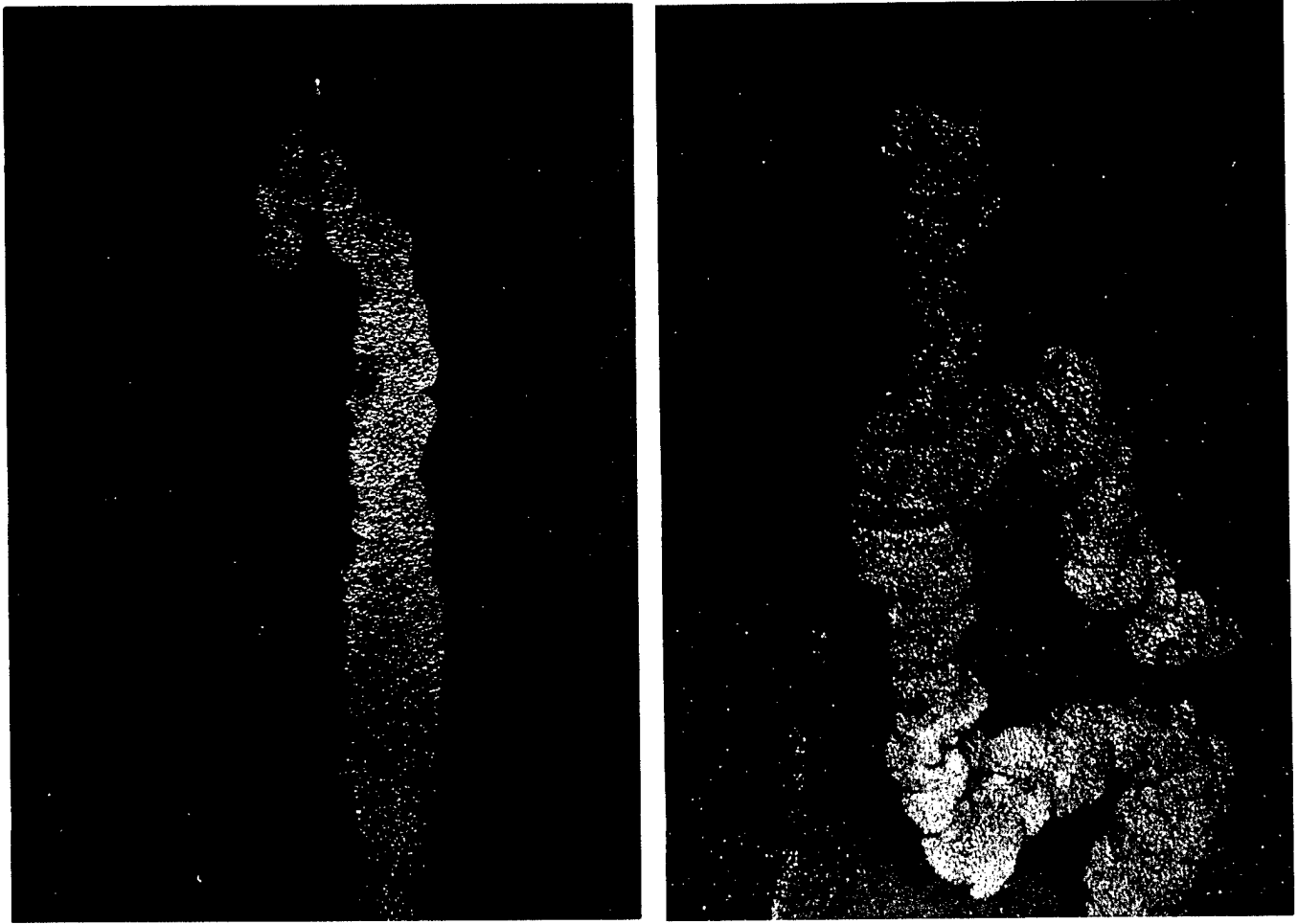


FIGURE 7 – Macrophotographs (8.5X) depicting examples of localized attack found (left) at scribed region and (right) elsewhere on fully coated (silane + ablative Cu) S31603 specimens.

APPENDIX 2

Photographic Documentation

APPENDIX 2

Photographic Documentation

Figure No.	Subject	Photo-Negative Identification
	In-Situ Views at 9 Months	
1.1	Tank #3 containing epoxy coated and silane (alone) coated specimens	2609-04-012-8
1.2	Tank #4 containing silane + ablative-Cu coated specimens	2609-04-012-12
1.3	Tank #5 as above + zinc anodes attached	2609-04-012-14
2.1	Affected N08367 panel with 20% epoxy coverage at 9 months	2609-04-012-6
2.2	Affected N08367 panel with 80% epoxy coverage at 9 months	2609-04-012-1
2.3	Blank	--
	Representative As-Removed Views of S31603 Specimens Exposed for 9 Months	
	<i>Epoxy Coverage</i>	
3.1	20% epoxy coated #114 (B)	2609-04-013-1
3.2	80% epoxy coated #118 (B)	2609-04-013-4
3.3	#114 (F) after brushing	2609-04-015-4A
	<i>Silane @ 20% Coverage</i>	
4.1	Silane A alone #44 (B)	2609-04-013-7
4.2	Silane B alone #56 (B)	2609-04-013-13
4.3	Silane C alone #67 (B)	2609-04-013-19
	<i>Silane @ 80% Coverage</i>	
5.1	Silane A alone #50 (B)	2609-04-013-10
5.2	Silane B alone #61 (B)	2609-04-013-16
5.3	Silane C alone #73 (B)	2609-04-013-22
	<i>Silane + Cu @ 20% Coverage</i>	
6.1	Silane A + Cu #78 (B)	2609-04-015-7A
6.2	Silane B + Cu #90 (B)	2609-04-015-14A
6.3	Silane C + Cu #102 (B)	2609-04-015-20A
	<i>Silane + Cu @ 80% Coverage</i>	
7.1	Silane A + Cu #84 (B)	2609-04-015-11A
7.2	Silane B + Cu #96 (B)	2609-04-015-17A
7.3	Silane C + Cu #108 (B)	2609-04-016-1

	<i>100% Coverage + Scribed Series Without Anodes</i>	
8.1	Silane A + Cu #24 (F)	2609-04-016-4
8.2	Silane B + Cu #32 (F)	2609-04-016-7
8.3	Silane C + Cu #36 (B)	2609-04-016-10
	<i>100% Coverage + Scribed Series With Zinc Anodes</i>	
9.1	Silane A + Cu #001 (F)	2609-04-017-15A
9.2	Silane B + Cu #107 (F)	2609-04-017-17A
9.3	Silane C + Cu #114 (F)	2609-04-017-19A
	Representative As-Removed Views of N08367 Specimens Exposed for 9 Months	
	<i>Epoxy Coverage</i>	
10.1	Attacked 20% epoxy coated #112 (B)	2609-04-014-1
10.2	Attacked 80% epoxy coated #118 (B)	2609-04-014-4A
10.3	Blank	--
	<i>Silane @ 20% Coverage</i>	
11.1	Silane A alone #44 (B)	2609-04-014-7A
11.2	Silane B alone #54 (B)	2609-04-014-13A
11.3	Silane C alone #66 (B)	2609-04-014-19A
	<i>Silane @ 80% Coverage</i>	
12.1	Silane A alone #48 (B)	2609-04-014-10A
12.2	Silane B alone #60 (B)	2609-04-014-16A
12.3	Silane C alone #72 (B)	2609-04-014-22A
	<i>Silane + Cu @ 20% Coverage</i>	
13.1	Silane A + Cu #78 (B)	2609-04-016-13
13.2	Silane B + Cu #90 (B)	2609-04-016-19
13.3	Silane C + Cu #102 (B)	2609-04-017-1
	<i>Silane + Cu @ 80% Coverage</i>	
14.1	Silane A + Cu #84 (B)	2609-04-016-16
14.2	Silane B + Cu #98 (B)	2609-04-016-22
14.3	Silane C + Cu #108 (B)	2609-04-017-3
	<i>100% Coverage + Scribed Series Without Anodes</i>	
15.1	Silane A + Cu #24 (B)	2609-04-017-6A
15.2	Silane B + Cu #30 (B)	2609-04-017-9A
15.3	Silane C + Cu #36 (B)	2609-04-017-12A

	<i>100% Coverage + Scribed Series With Zinc Anodes</i>	
16.1	Silane A + Cu +001 (F)	2609-04-017-16A
16.2	Silane B + Cu #107 (F)	2609-04-017-18A
16.3	Silane C + Cu #114 (F)	2609-04-017-20A
17.1	Blank	--
17.2	Blank	--
17.3	Blank	--
	After-Cleaning Views of Epoxy Coated S31603 Specimens	
	<i>20% Coverage – 9 Months</i>	
18.1	Left-right: #112, #113 and #114 (front views)	2609-04-019-1A
18.2	As above (back views)	2609-04-019-4
18.3	Comparative worst case view of (top) 3-month specimen #020 (B) and (bottom) 9-month specimen #113 (F)	2609-04-023-5
	<i>80% Coverage – 9 Months</i>	
19.1	Left-right: #118, #119 and #120 (front views)	2609-04-019-7
19.2	As above (back views)	2609-04-019-10
19.3	Comparative worst case view of (top) 3-month specimen #116 (B) and (bottom) 9-month specimen #120 (F)	2609-04-023-8
	After-Cleaning Views of Epoxy Coated N08367	
	<i>20% Coverage – 9 Months</i>	
20.1	Left-right: #112, #113 and #114 (front views)	2609-04-019-13
20.2	As above (back views)	2609-04-019-16
20.3	Comparative worst case view of (top) 3-month specimen #111 (B) and (bottom) 9-month specimen #112 (B)	2609-04-023-11
	<i>80% coverage – 9 months</i>	
21.1	Left-right: #118, #119 and #120 (front views)	2609-04-019-19
21.2	As above (back views)	2609-04-019-22
21.3	Comparative worst case view of (top) 3-month specimen #116 (B) and (bottom	2609-04-023-14
	After-Cleaning Views of Silane (alone) Coated S31603 Specimens	
	<i>20% Coverage</i>	
22.1	Silane A, left-right: #42B, #43F and #43B	2609-04-020-1
22.2	Silane B, left-right: #54B, #55B and #56B	2609-04-020-7
22.3	Silane C, left-right: #66F, #67B and #68B	2609-04-020-13

	<i>80% Coverage</i>	
23.1	Silane A, left-right: #48F, #49F and #50F	2609-04-020-4
23.2	Silane B, left-right: #60F, #61F and #62F	2609-04-020-10
23.3	Silane C, left-right: #72F, #73F and #74F	2609-04-020-16
	After-Cleaning Views of Silane (alone) Coated N08367 Specimens	
	<i>All Front Side Views – 20% Coverage</i>	
24.1	Silane A, Left-right: #42, #43 and #44	2609-04-020-19
24.2	Silane B, left-right: #54, #55 and #56	2609-04-021-1
24.3	Silane C, left-right: #66, #67 and #68	2609-04-021-7
	<i>All Front Side Views – 80% Coverage</i>	
25.1	Silane A, left-right: #48, #49 and #50	2609-04-020-22
25.2	Silane B, left-right: #60, #61 and #62	2609-04-021-4
25.3	Silane C, left-right: #72, #73 and #74	2609-04-021-10
	After-Cleaning Views of Silane + Ablative-Cu Coated Specimens	
	<i>Worst Case Examples of Attack For S31603 Specimens (left-right) Pretreated with Silane A, B and C</i>	
26.1	20% coverage #079 (F), #090 (B) and #102 (F)	2609-04-018-10
26.2	80% coverage #085 (B), #096 (F) and #108 (F)	2609-04-018-13
26.3	100% coverage + scribed #024 (F), #030 (F) and #036 (F)	2609-04-018-16
	<i>Representative Views of Resistant N08367 Specimens (left-right) Pretreated with Silane A, B and C</i>	
27.1	20% coverage #078 (F), #090 (F) and #102 (F)	2609-04-018-1
27.2	80% coverage #084 (F), #098 (F) and #108 (F)	2609-04-018-4
27.3	100% coverage + scribed #024 (F), #030 (F) and #036 (F)	2609-04-018-7
	Effect of Test Duration Worst Case Examples from (left) Nine-Month Test and (right) 3-Month Test	
	<i>S31603 Series with 20% Coverage – Silane + Ablative-Cu</i>	
28.1	Silane A Pretreatment (#079 back and #077 back)	2609-04-022-2A
28.2	Silane B Pretreatment (#091 back and #089 back)	2609-04-022-8A
28.3	Silane C Pretreatment (#102 front and #099 front)	2609-04-022-14A
	<i>S31603 Series with 80% Coverage – Silane + Ablative-Cu</i>	
29.1	Silane A Pretreatment (#085 back and #081 front)	2609-04-022-5A
29.2	Silane B Pretreatment (#097 front and #094 front)	2609-04-022-11A
29.3	Silane C Pretreatment (#108 front and #106 front)	2609-04-022-17A

	Select Close-up Views of Attacked S31603 Specimens Partially Coated with Silane + Ablative-Cu	
	<i>Worst Case Examples (Left-right) 9-months and 3-months</i>	
30.1	Silane B @ 20% #087 (front) – exposed for 3 months	2609-04-024-20
30.2	Silane B @ 20% #091 (front) – exposed for 9 months	2609-04-025-2
30.3	Silane B @ 20% #091 (back) – exposed for 9 months	2609-04-024-23
	S31603 Series with 100% Coverage Silane + Ablative-Cu and Scribed	
31.1	Silane A Pretreatment (#024 front and #022 front)	2609-04-022-20A
31.2	Silane B Pretreatment (#032 back and #028 front)	2609-04-022-23A
31.3	Silane C Pretreatment (#036 back and #035 front)	2609-04-023-2
32.1	Example of scribed related attack – shown Silane A specimen #024 (front)	2609-04-024-17
	Representative Views of Fully Coated + Scribed Specimens Exposed with Cathodic Protection for 9 Months	
32.2	S31603 Series (left-right) pretreated with Silane A (#001), B (#009) and C (#013)	2609-04-018-19
32.3	N08367 Series (left-right) pretreated with Silane A (#002), B (#007) and C (#015)	2609-04-018-22
33.1	Close-up view of cathodically protected N08367 specimen #004 (front) originally pretreated with Silane A and exposed for 9 months	2609-04-024-14
33.2	Close-up view of freely corroding N08367 specimen #024 (front) originally pretreated with Silane A and exposed for 9 months	2609-04-024-8

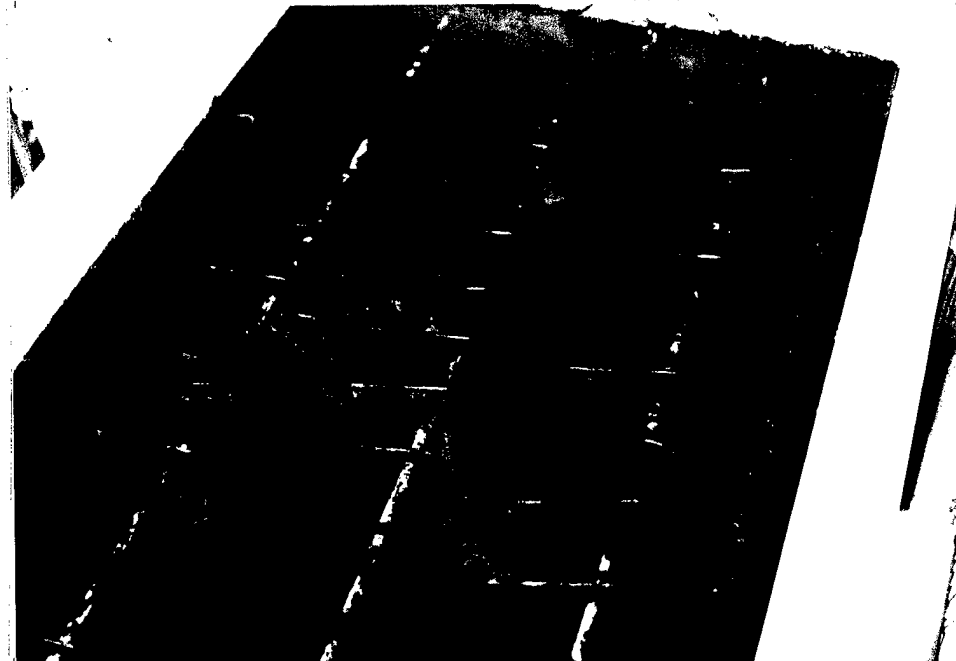


Figure 1.1 2609-04-012-8

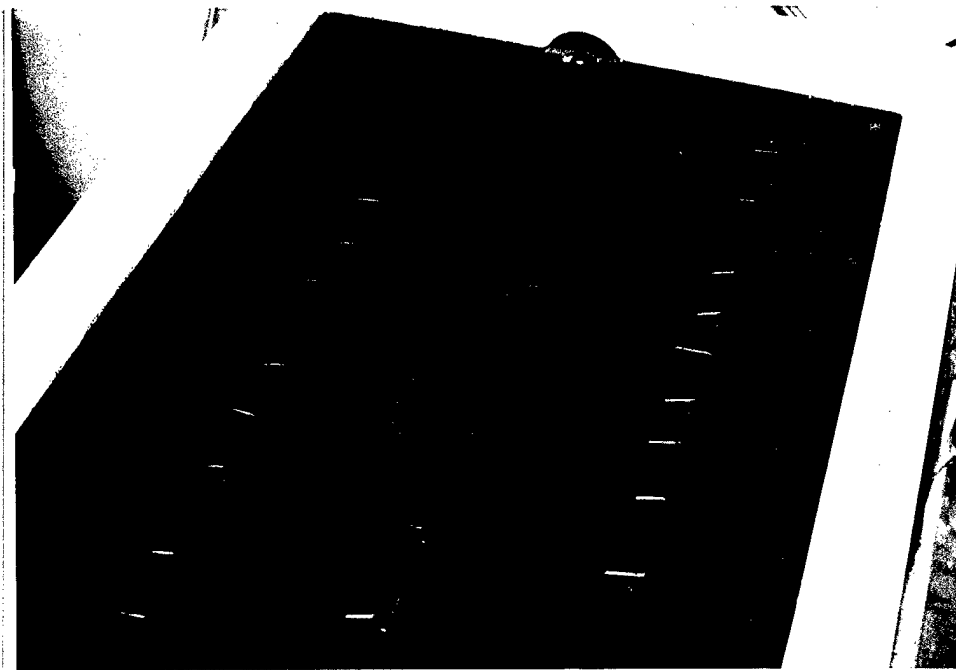


Figure 1.2 2609-04-012-12

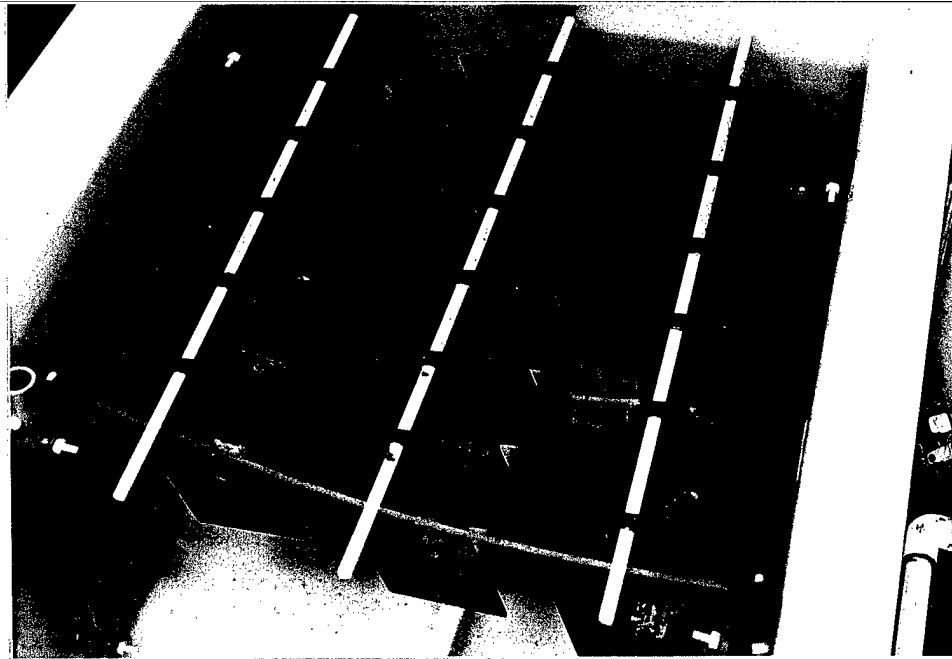


Figure 1.3 2609-04-012-14

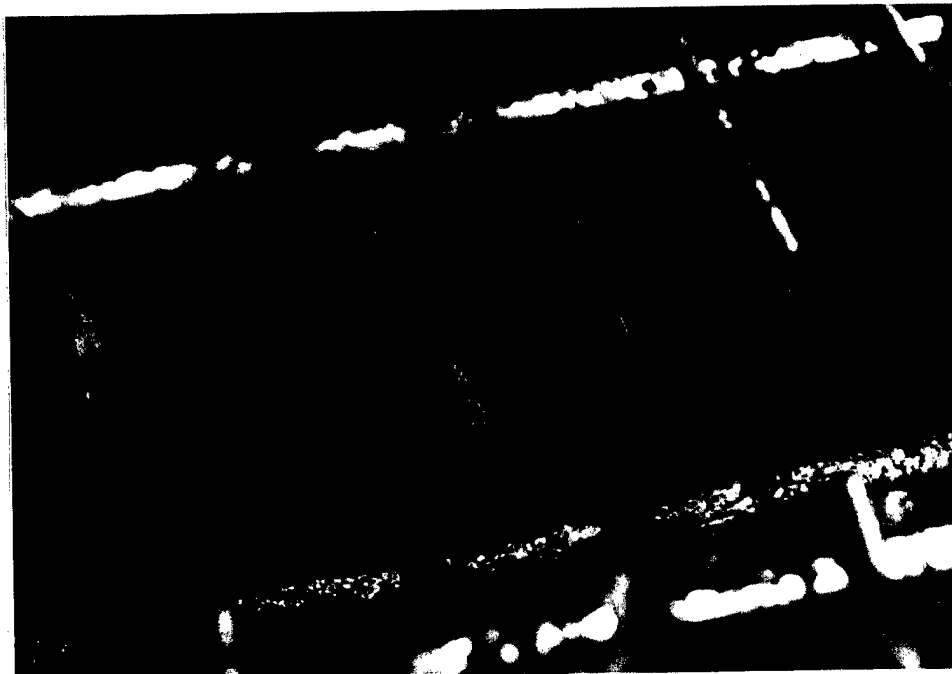


Figure 2.1 2609-04-012-6



Figure 2.2 2609-04-012-1

Figure 2.3 Blank



Figure 3.1 2609-04-013-1

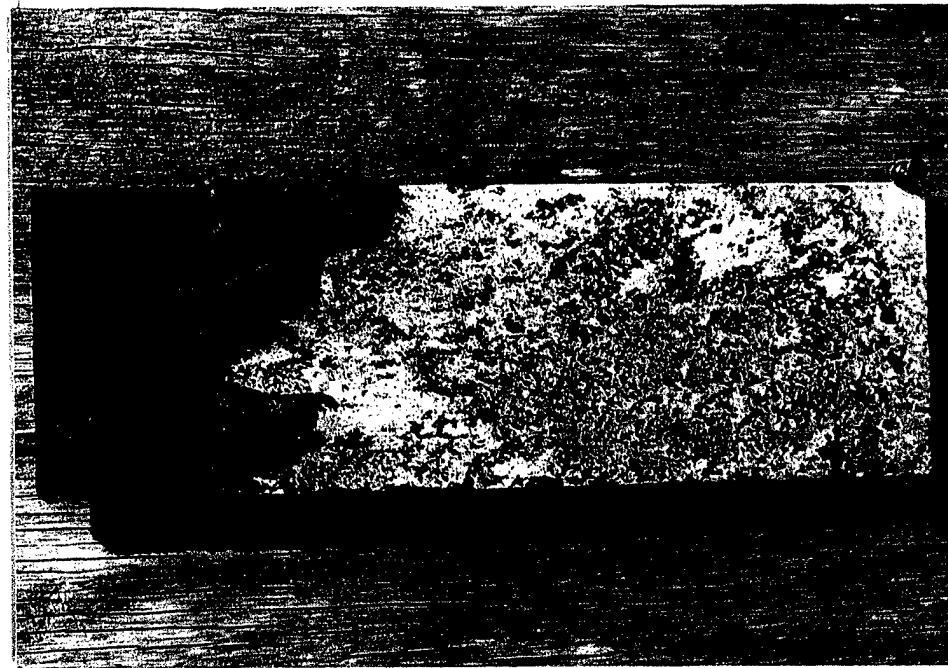


Figure 3.2 2609-04-013-4

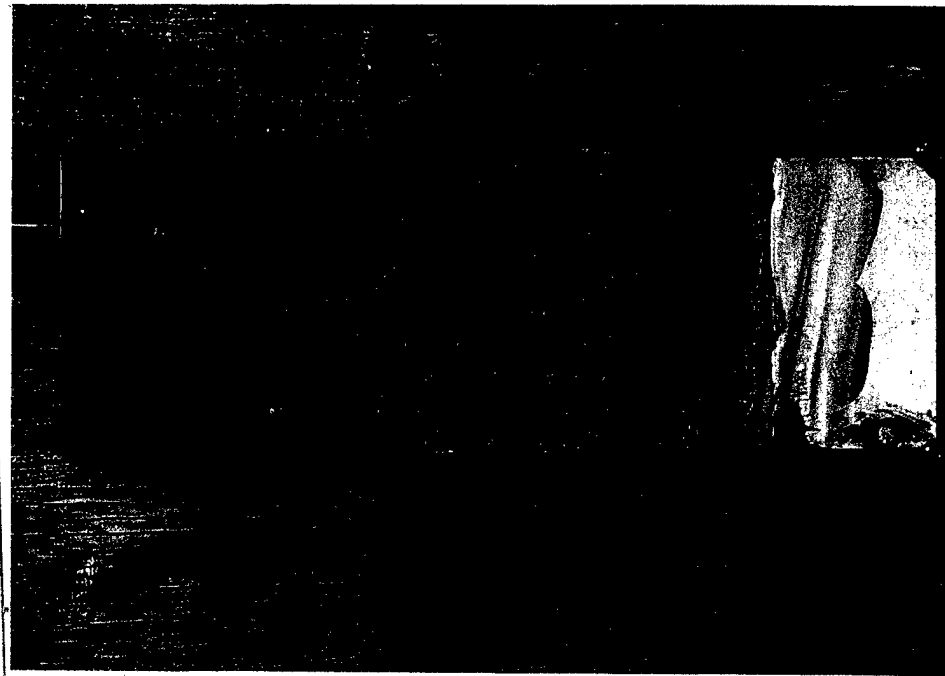


Figure 3.3 2609-04-015-4A

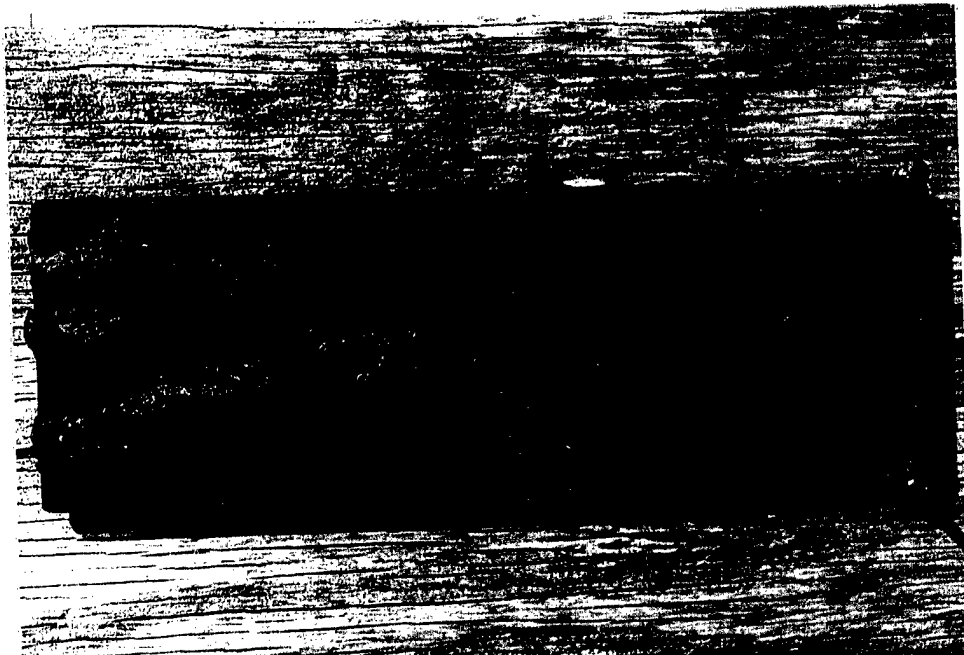


Figure 4.1 2609-04-013-7

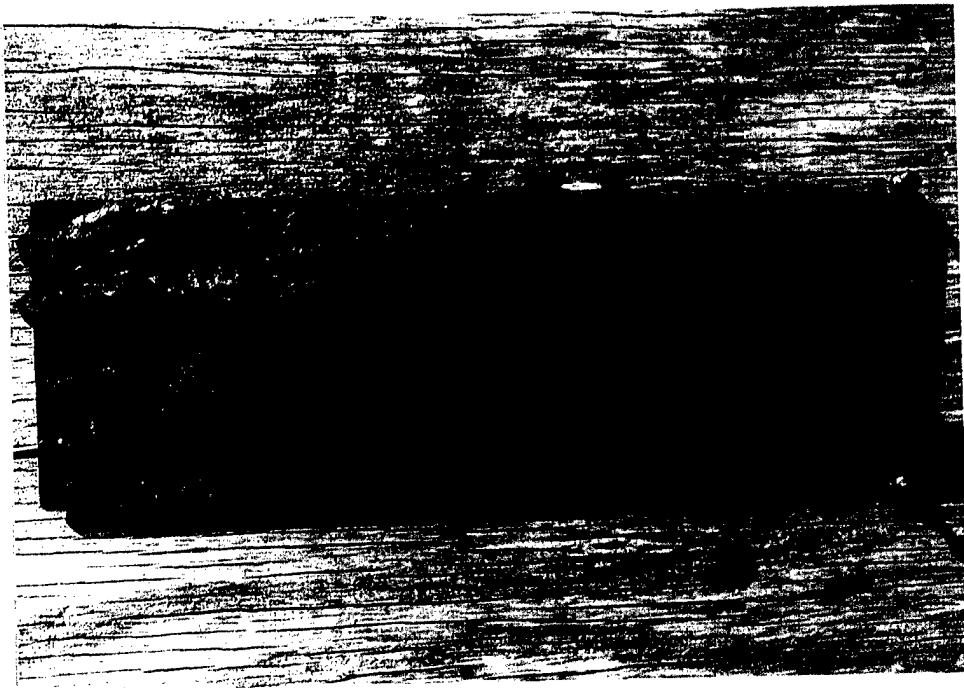


Figure 4.2 2609-04-013-13



Figure 4.3 2609-04-013-19

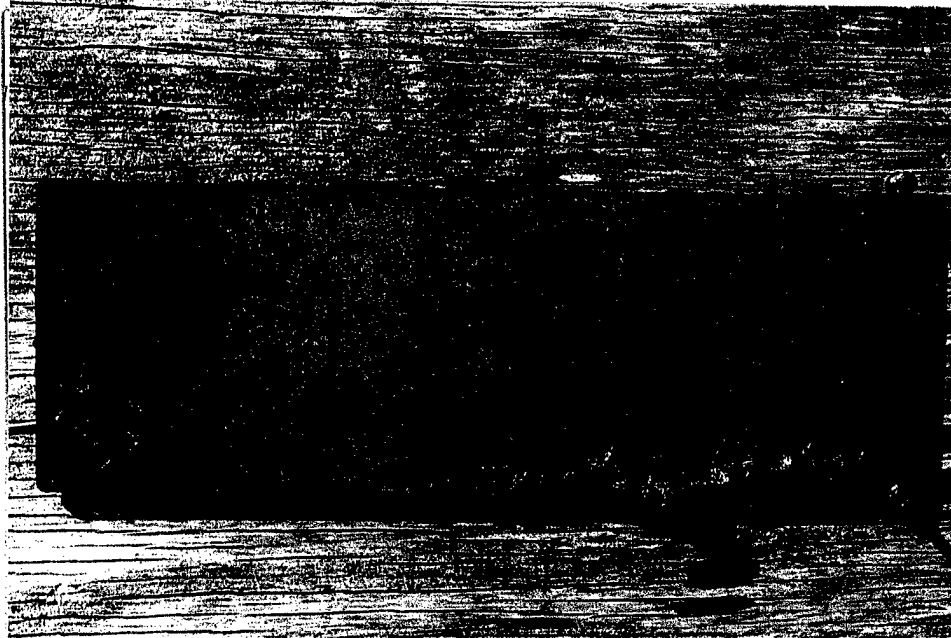


Figure 5.1 2609-04-013-10



Figure 5.2 2609-04-013-16



Figure 5.3 2609-04-013-22

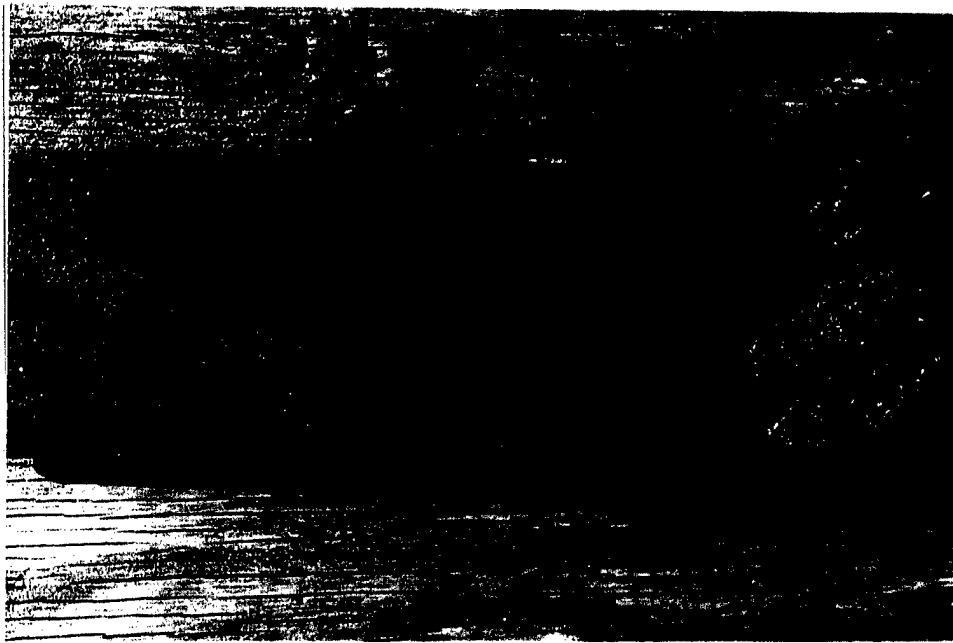


Figure 6.1 2609-04-015-7A

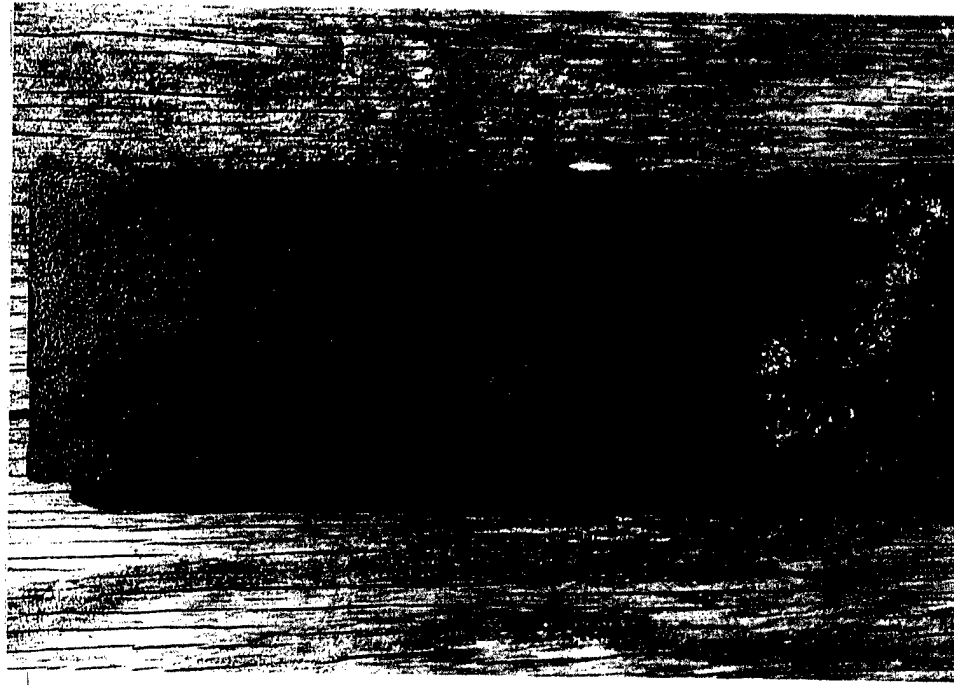


Figure 6.2 2609-04-015-14A

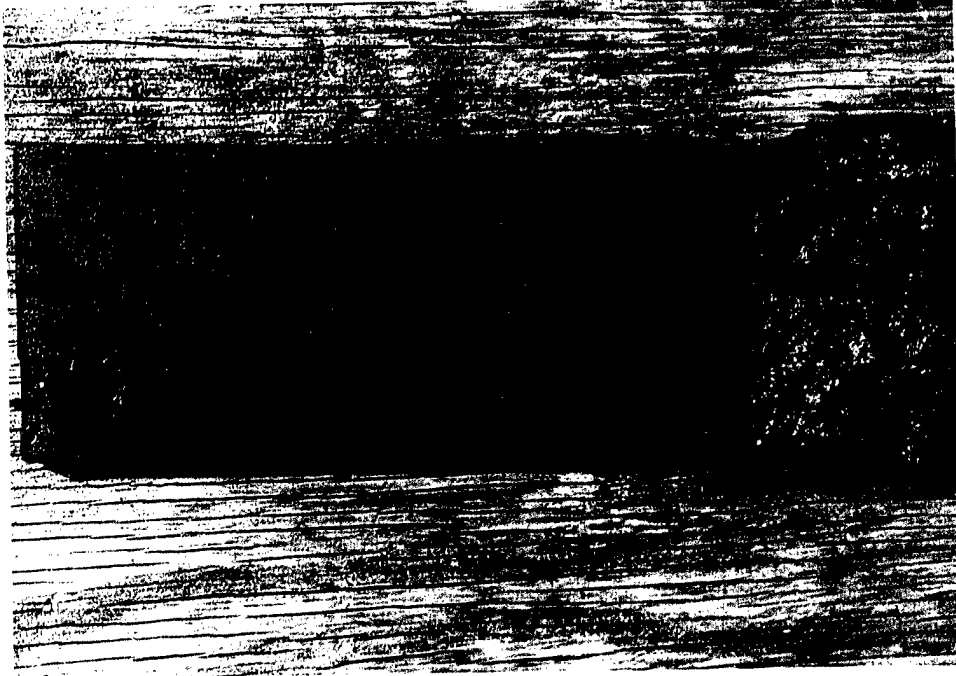


Figure 6.3 2609-04-015-20A

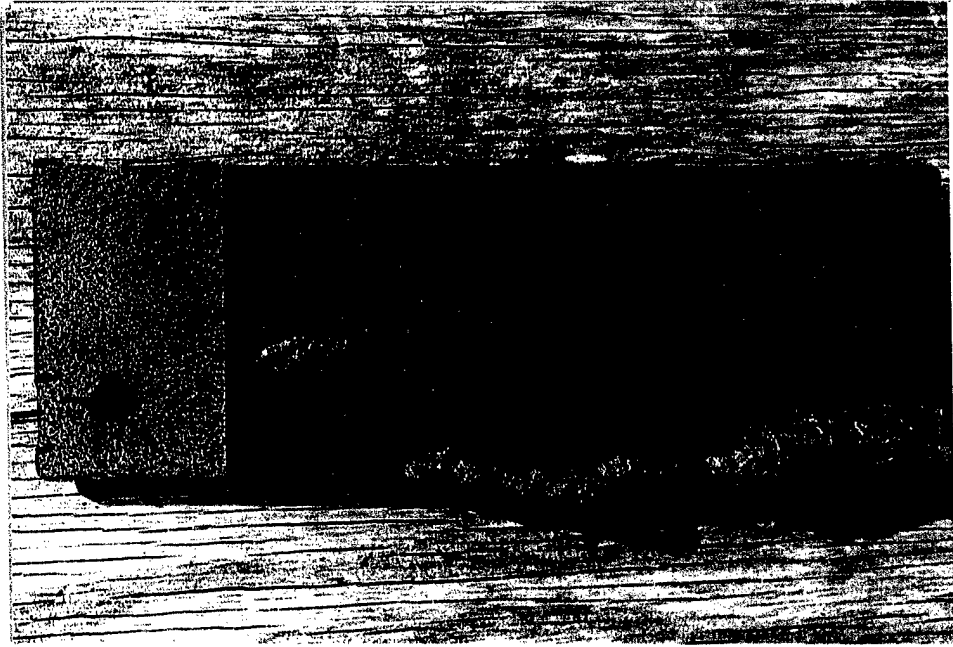


Figure 7.1 2609-04-015-11A

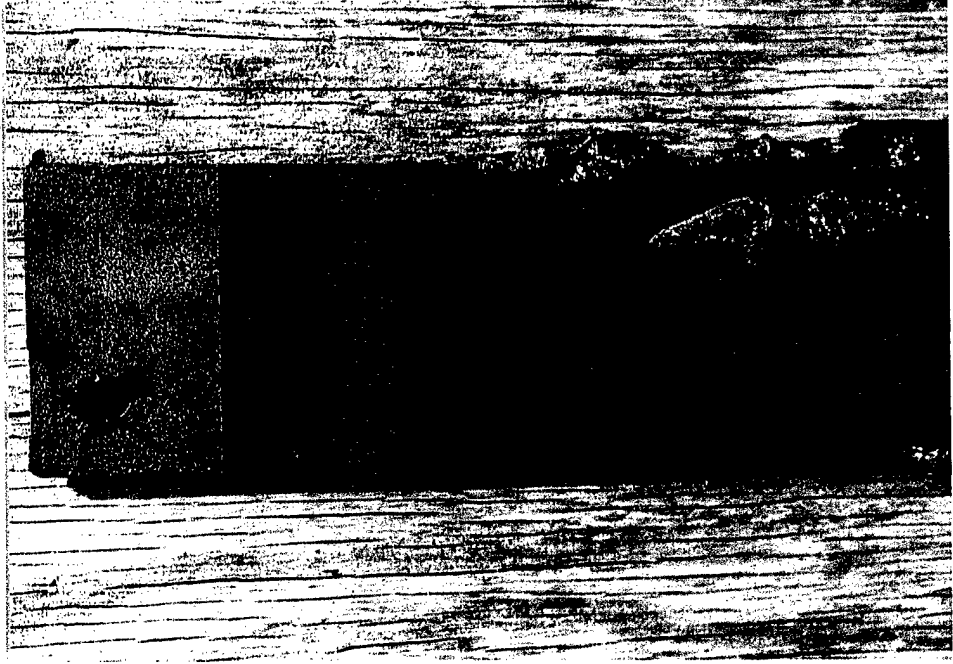


Figure 7.2 2609-04-015-17A



Figure 7.3 2609-04-016-1



Figure 8.1 2609-04-016-4

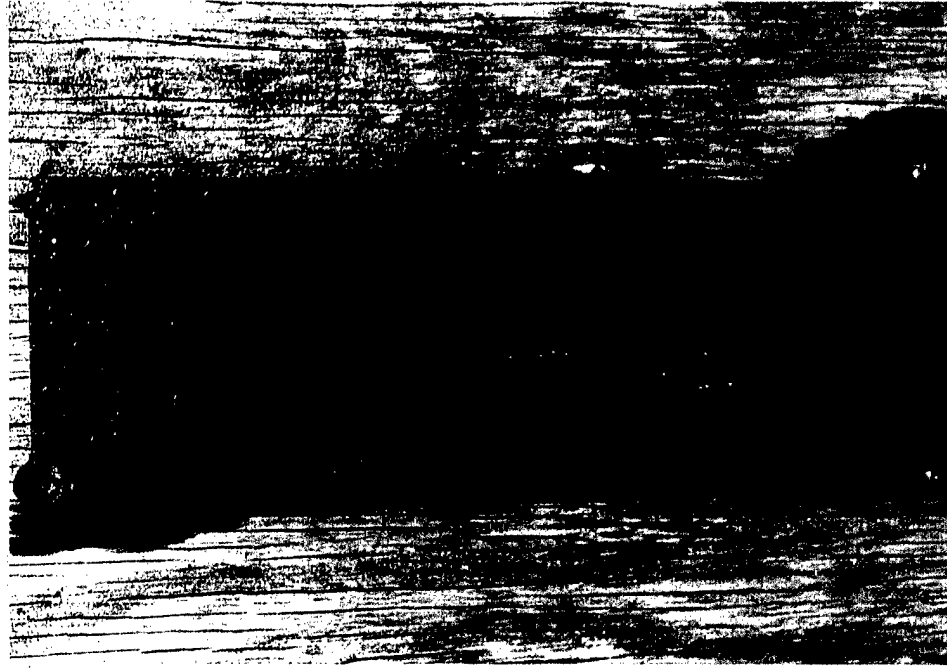


Figure 8.2 2609-04-016-7



Figure 8.3 2609-04-016-10



Figure 9.1 2609-04-017-15A

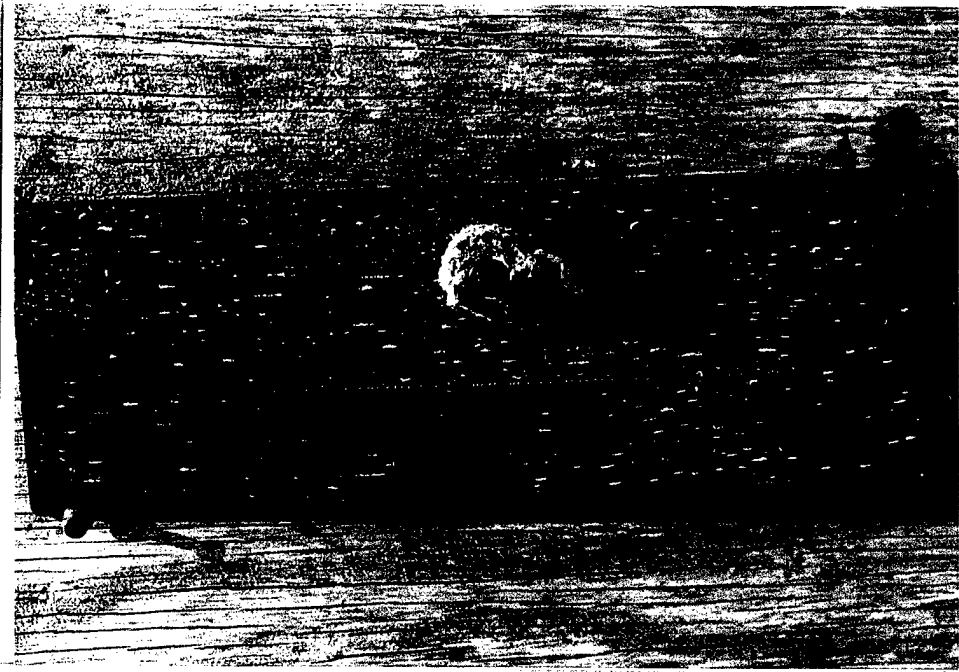


Figure 9.2 2609-04-017-17A

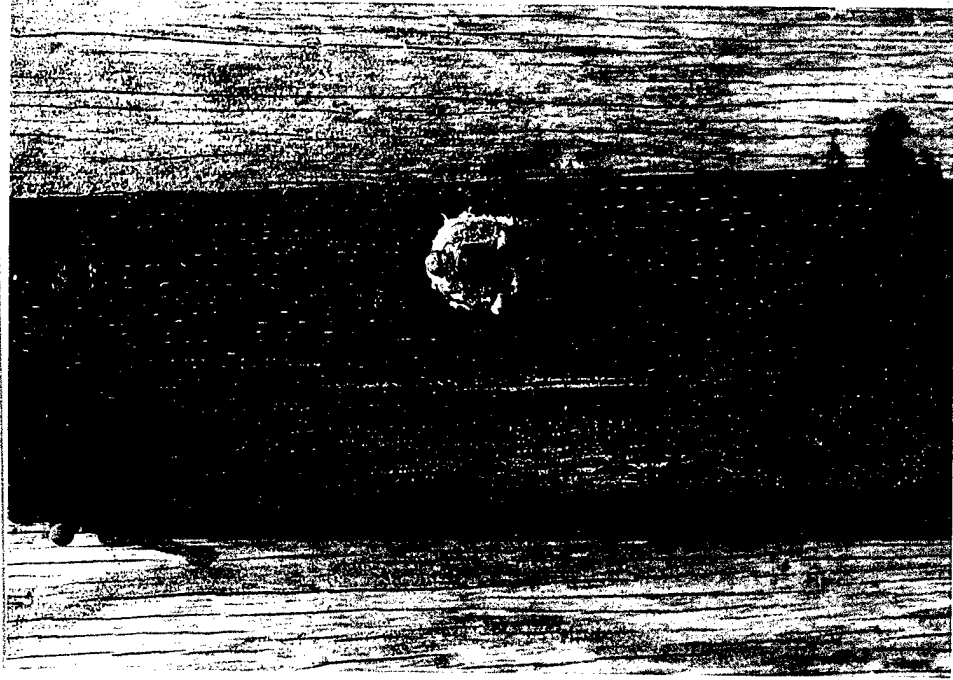


Figure 9.3 2609-04-017-19A

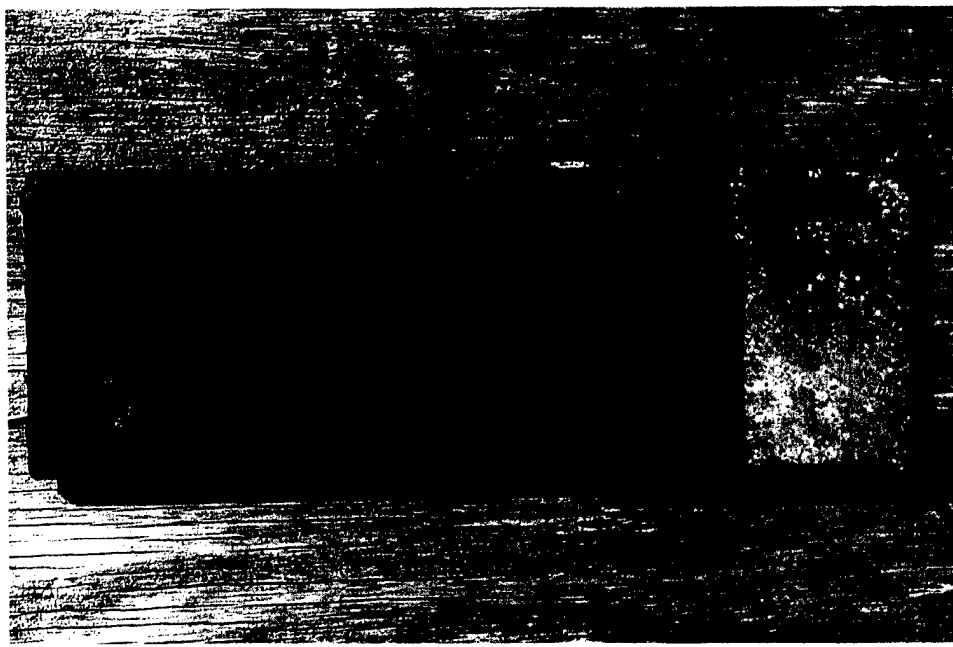


Figure 10.1 2609-04-014-1

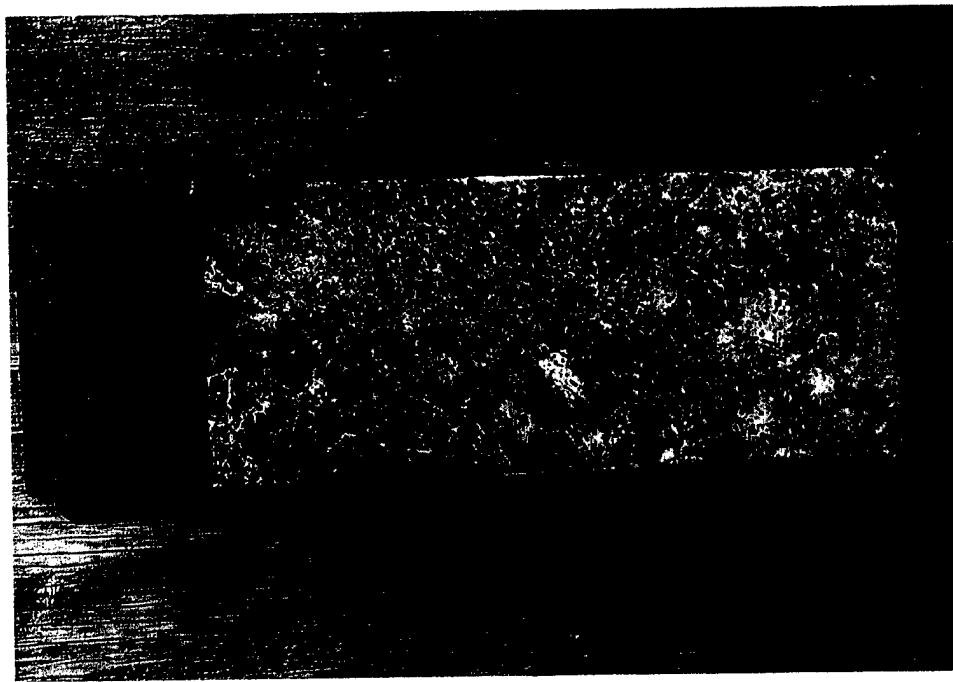


Figure 10.2 2609-04-014-4A

Figure 10.3 Blank

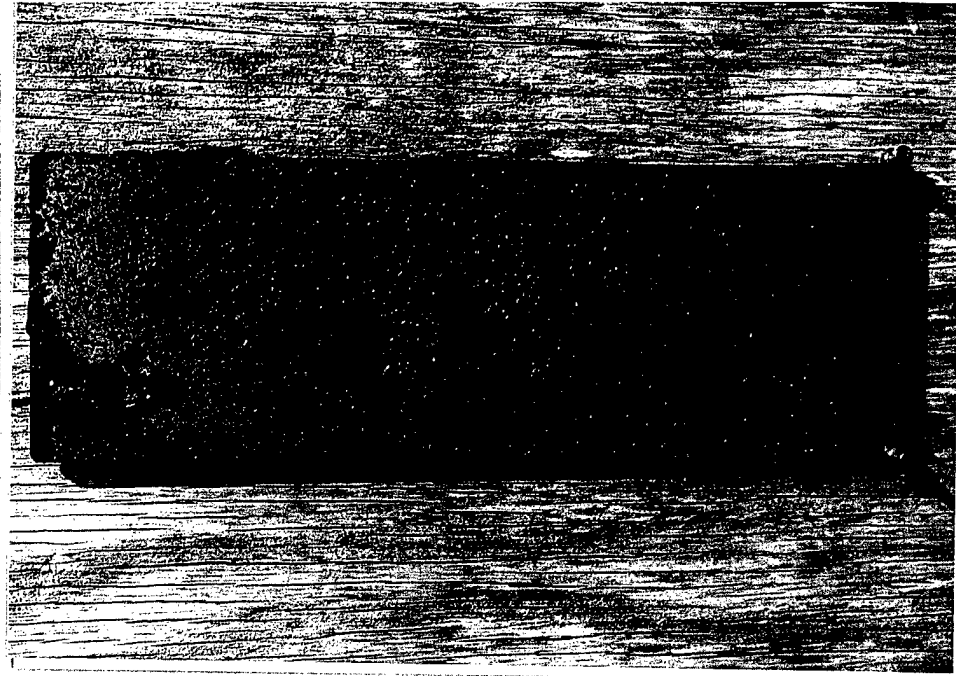


Figure 11.3 2609-04-014-19A

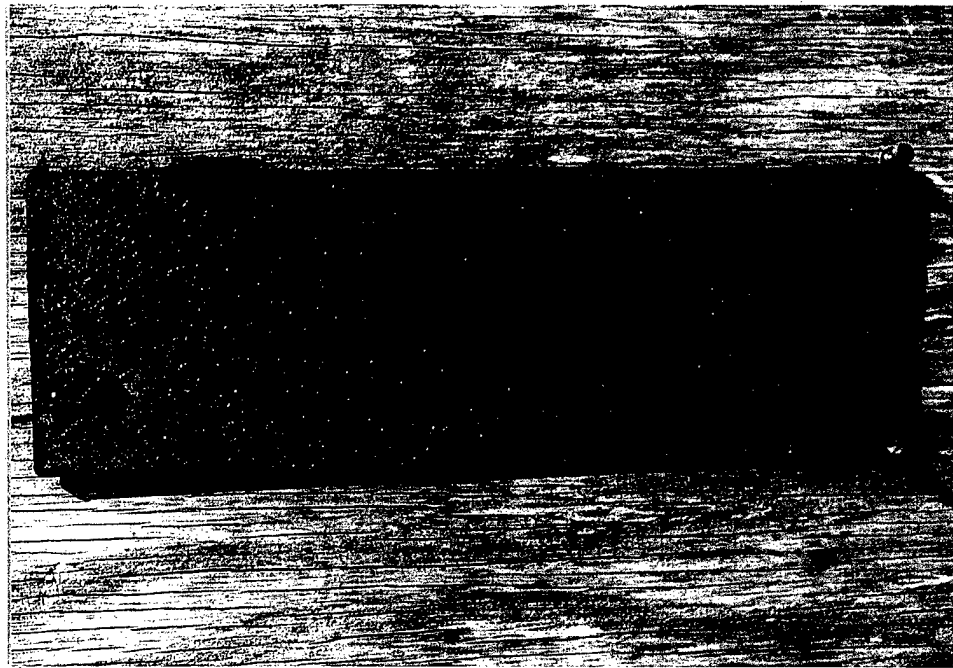


Figure 11.2 2609-04-014-13A

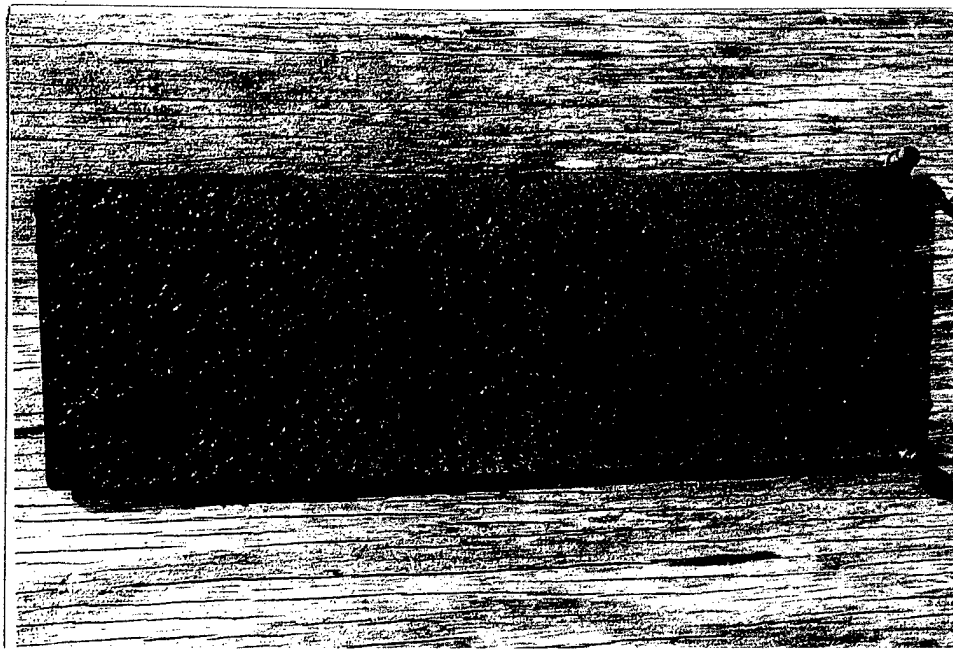


Figure 11.1 2609-04-014-7A

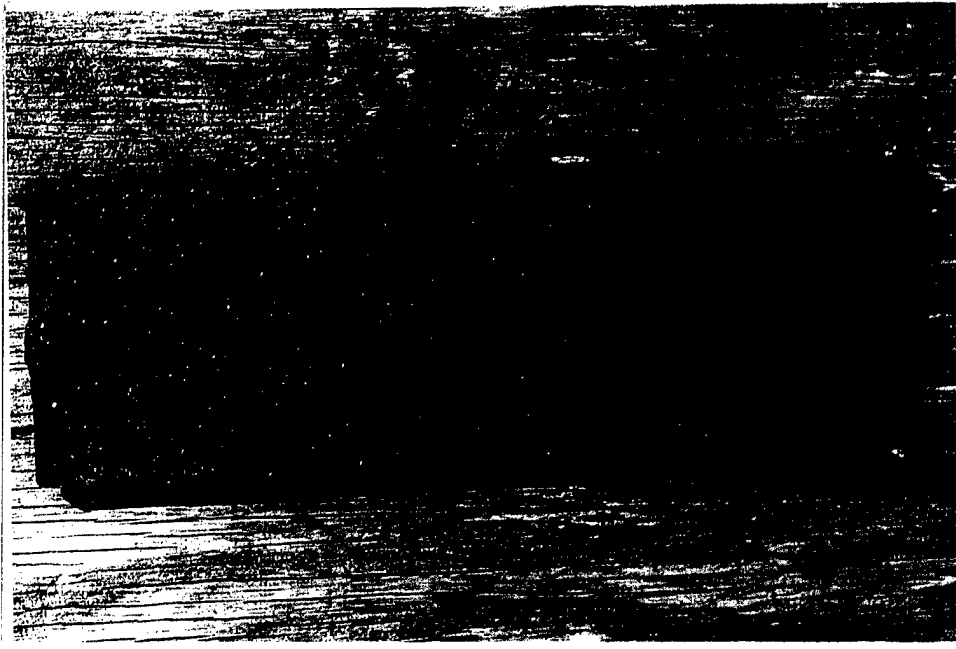


Figure 12.1 2609-04-014-10A

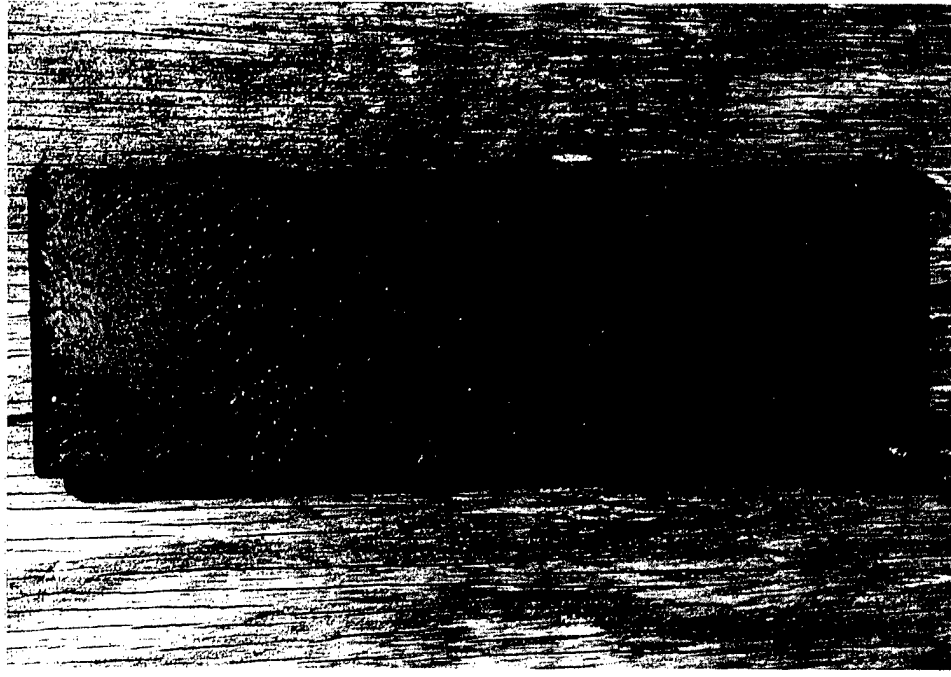


Figure 12.2 2609-04-014-16A

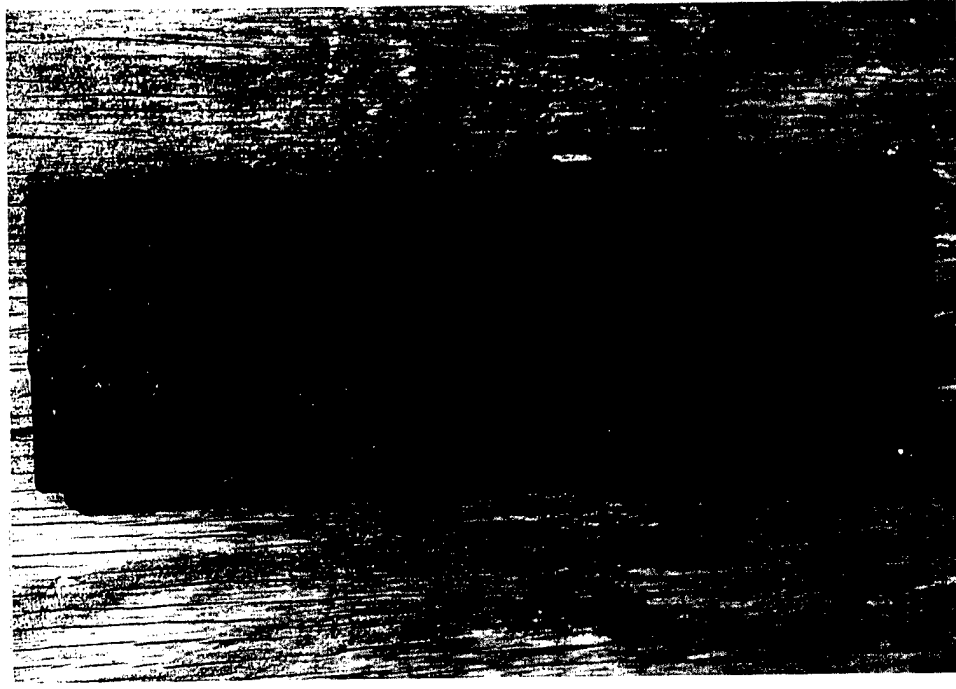


Figure 12.3 2609-04-014-22A

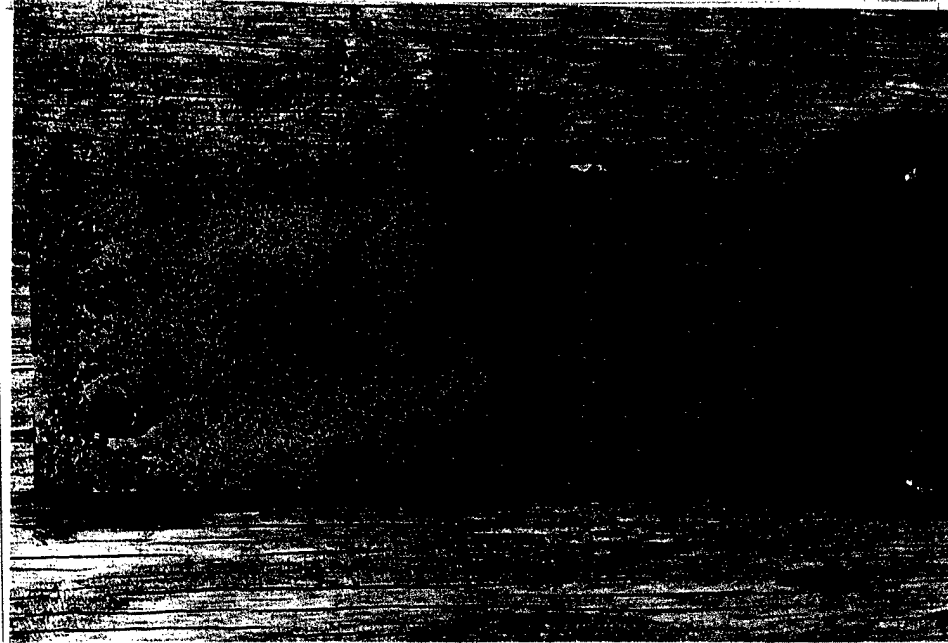


Figure 13.1 2609-04-016-13

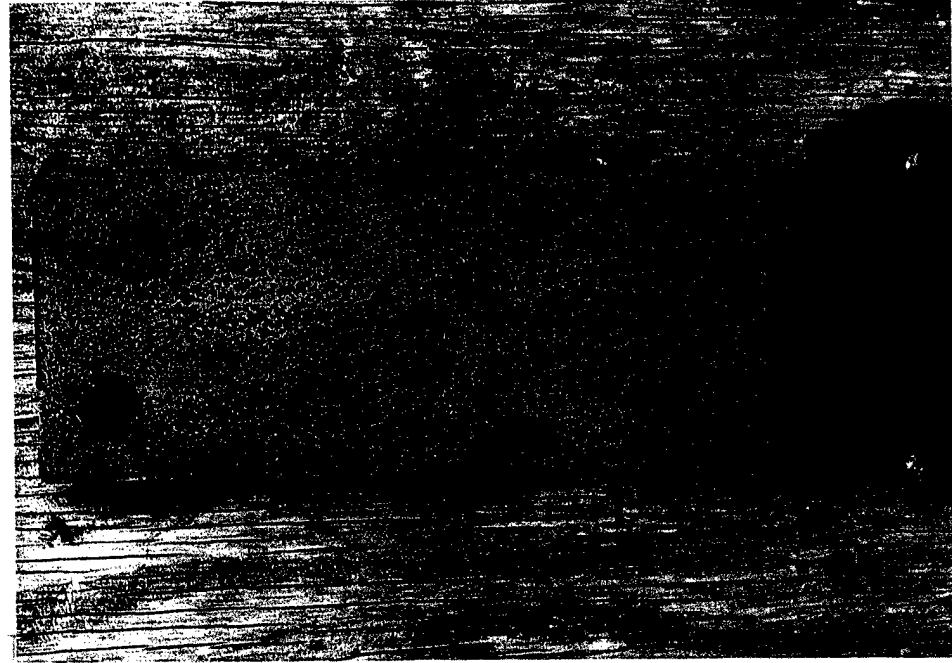


Figure 13.2 2609-04-016-19



Figure 13.3 2609-04-017-1

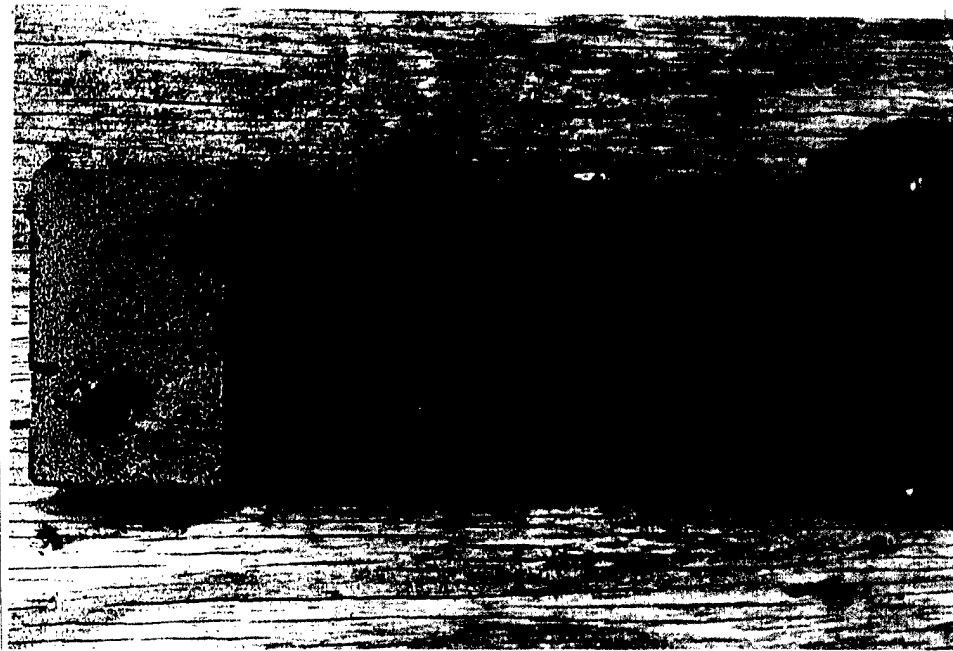


Figure 14.1 2609-04-016-16

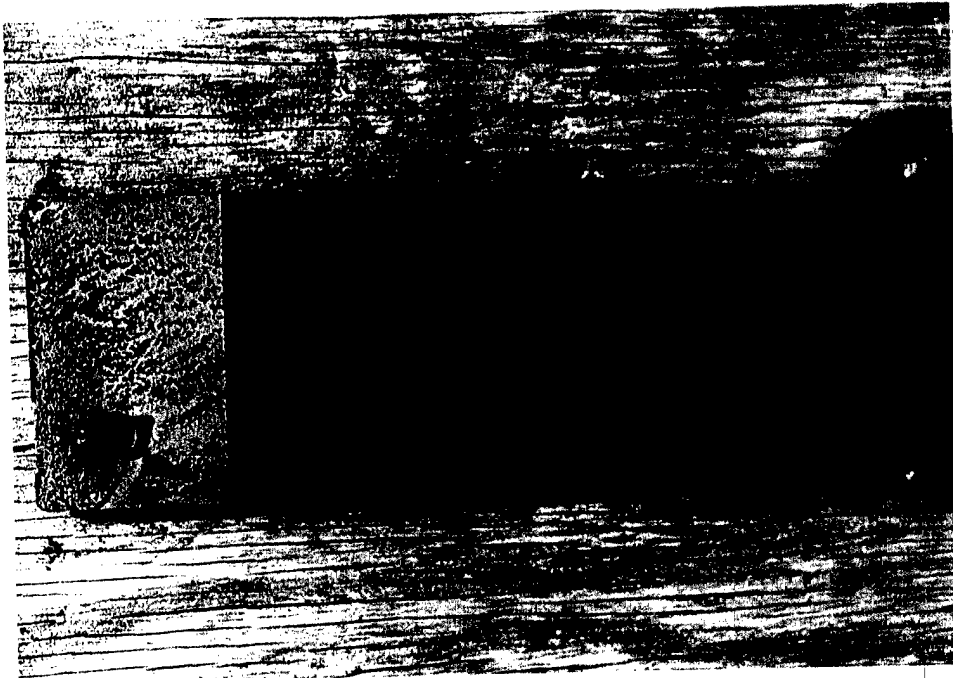


Figure 14.2 2609-04-016-22



Figure 14.3 2609-04-017-3

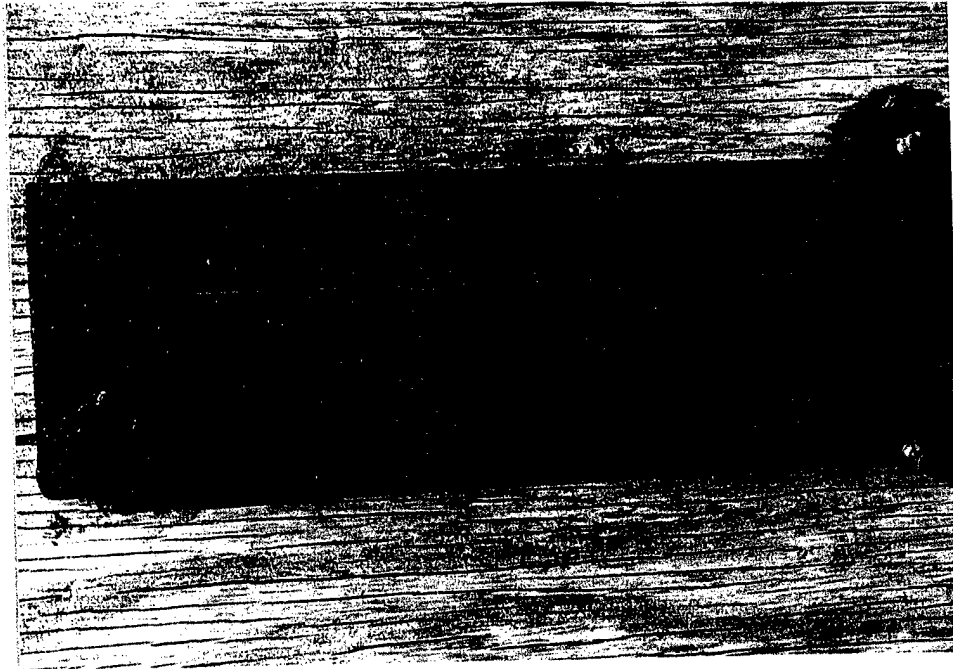


Figure 15.1 2609-04-017-6A



Figure 15.2 2609-04-017-9A

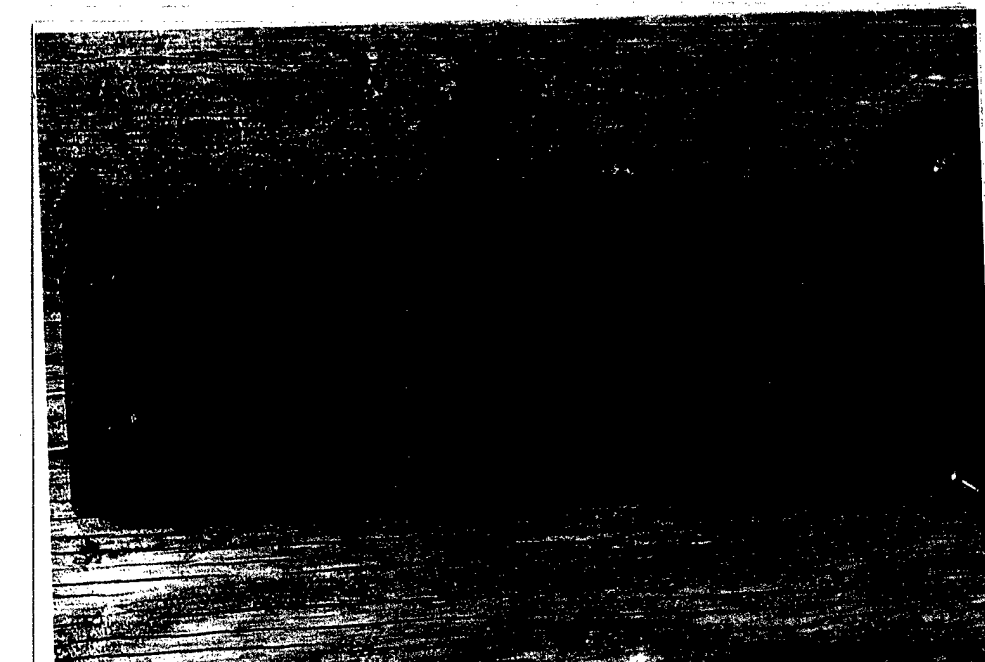


Figure 15.3 2609-04-017-12A



Figure 16.1 2609-04-017-16A

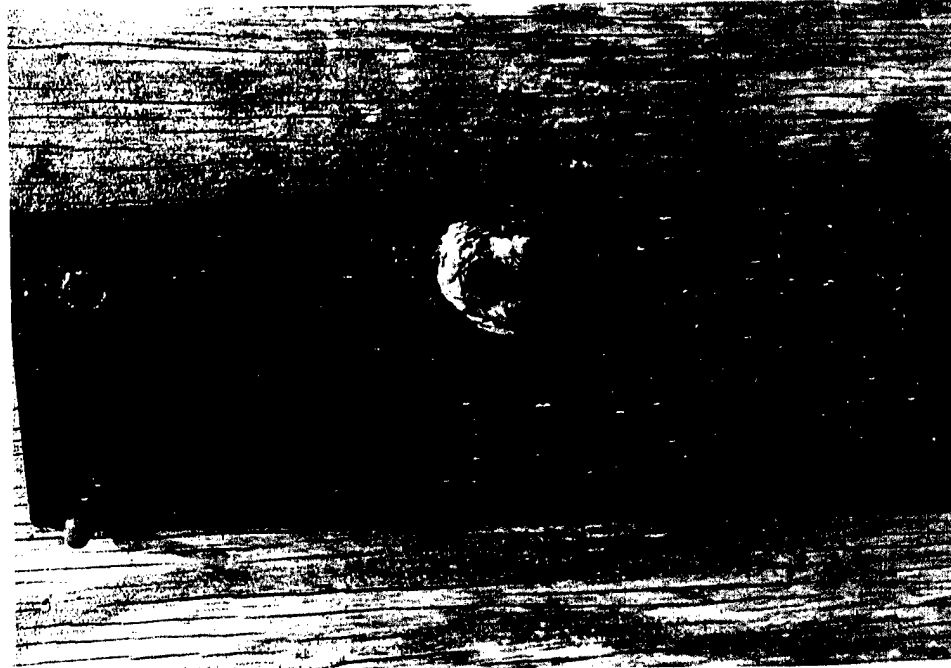


Figure 16.2 2609-04-017-18A



Figure 16.3 2609-04-017-20A

Figure 17.1 Blank

Figure 17.2 Blank

Figure 17.3 Blank

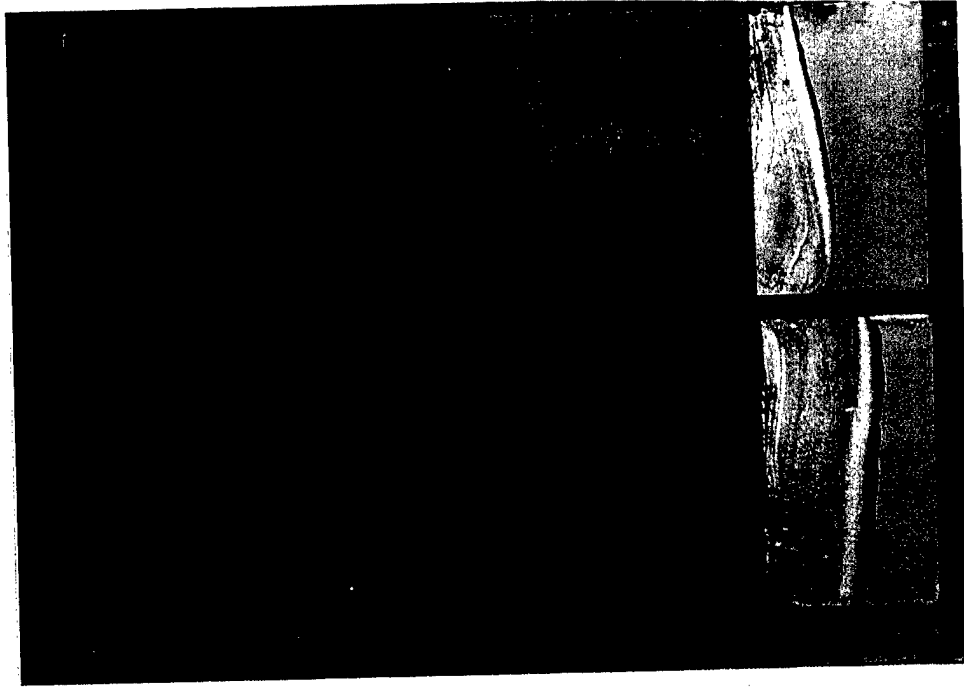


Figure 18.3 2609-04-023-5

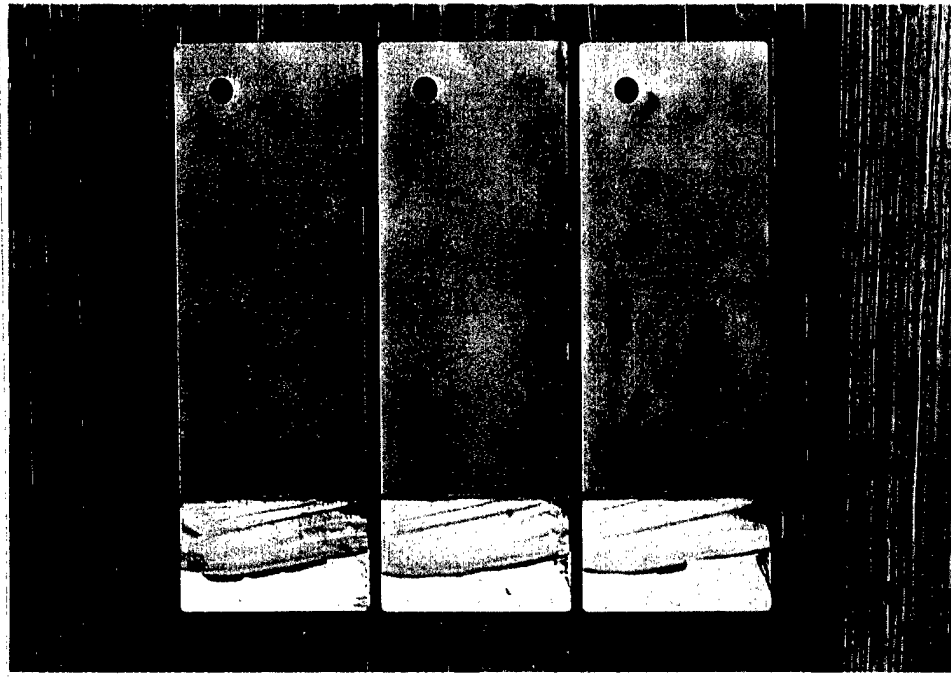


Figure 18.1 2609-04-019-4



Figure 18.1 2609-04-019-1A

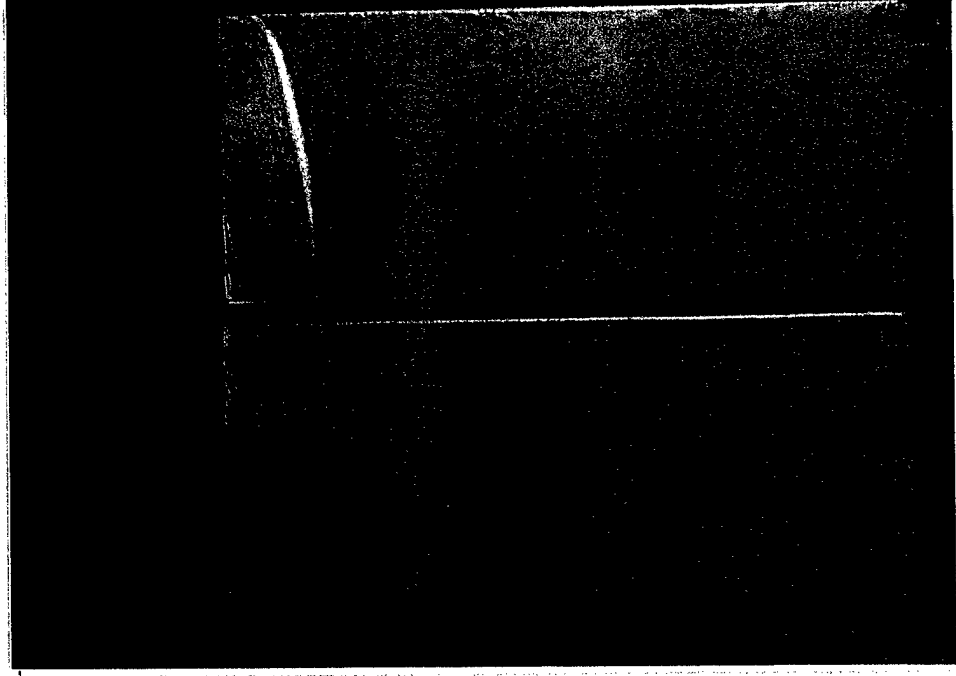


Figure 19.3 2609-04-023-8

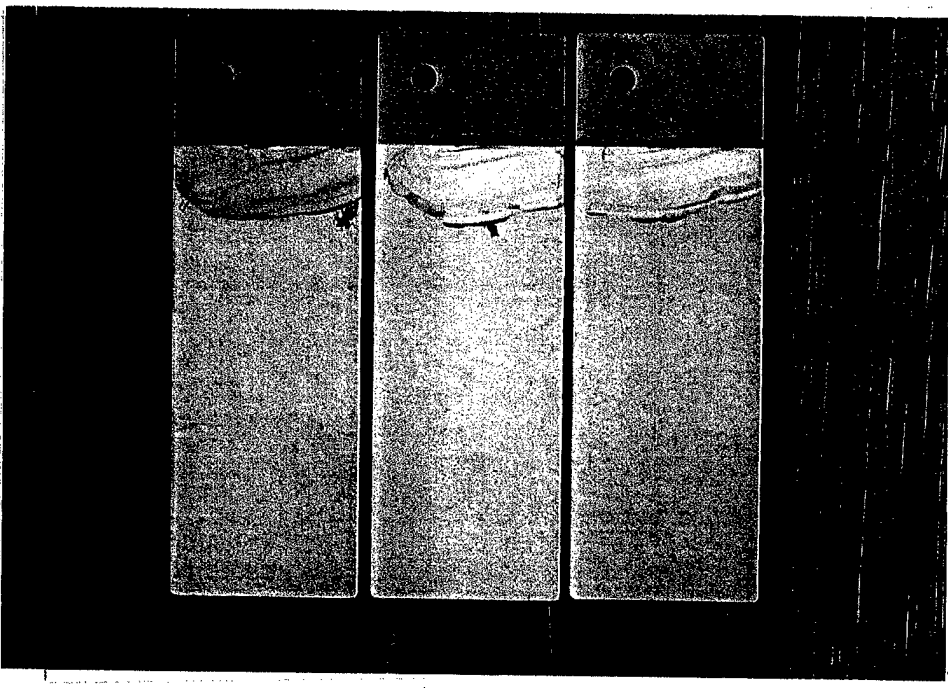


Figure 19.2 2609-04-019-10

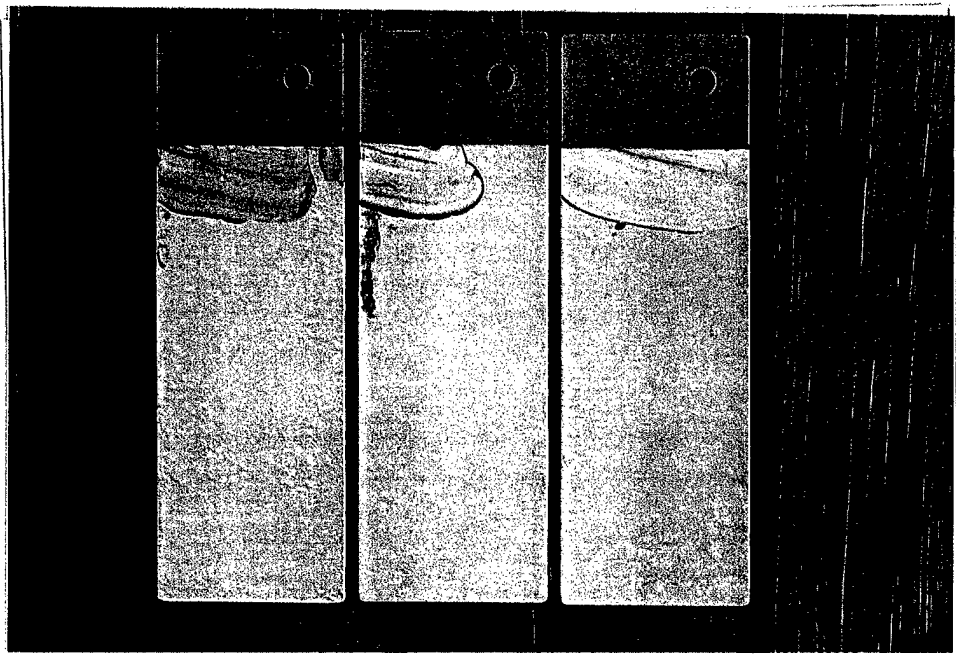


Figure 19.1 2609-04-019-7

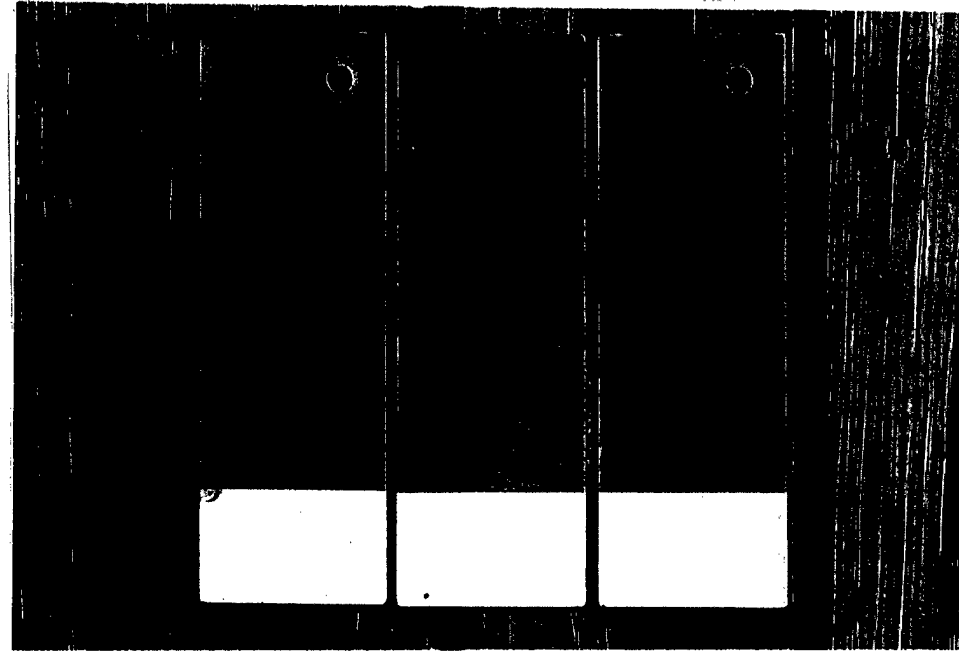


Figure 20.1 2609-04-019-13

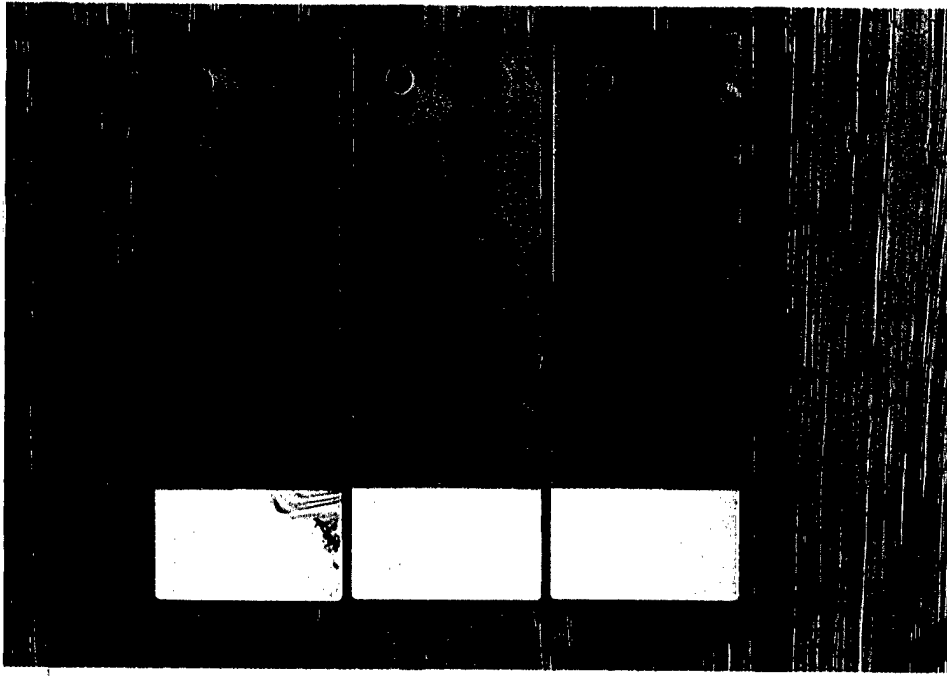


Figure 20.2 2609-04-019-16

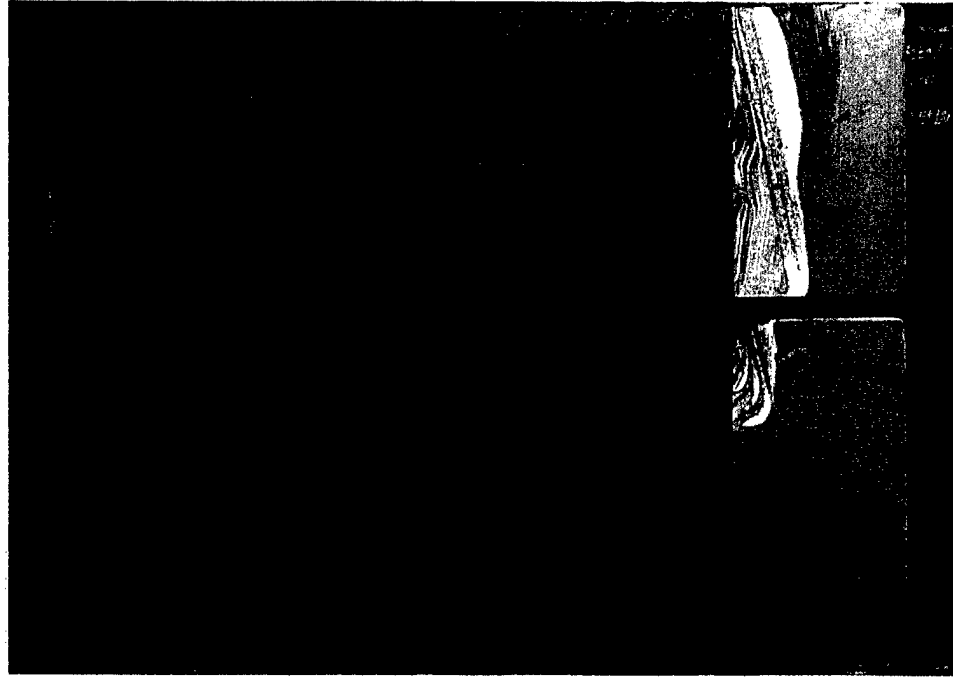


Figure 20.3 2609-04-023-11

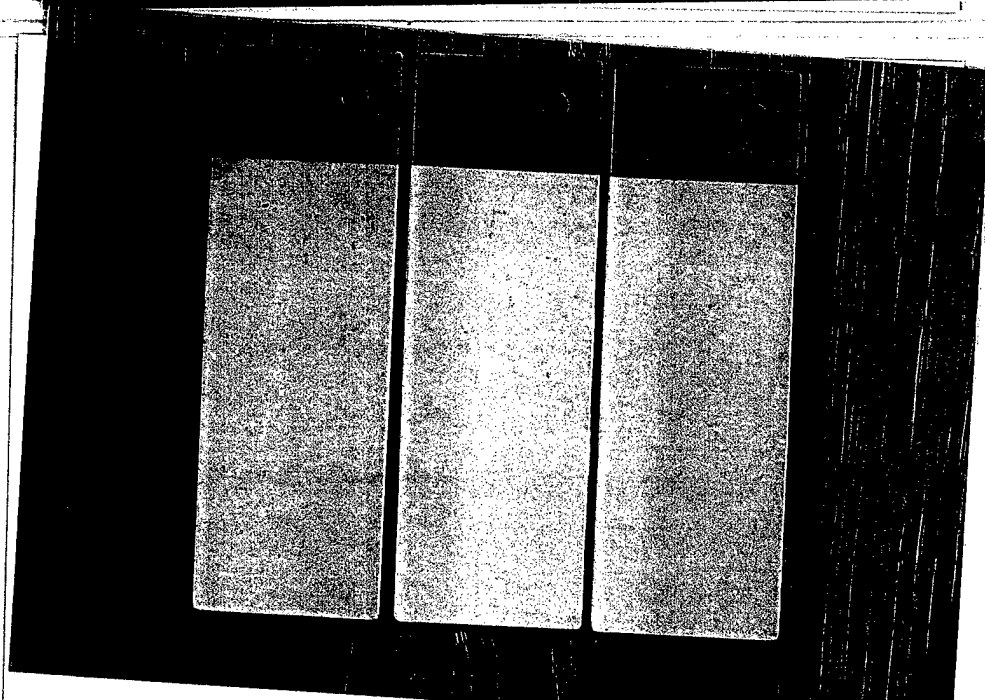


Figure 21.1 2609-04-019-19

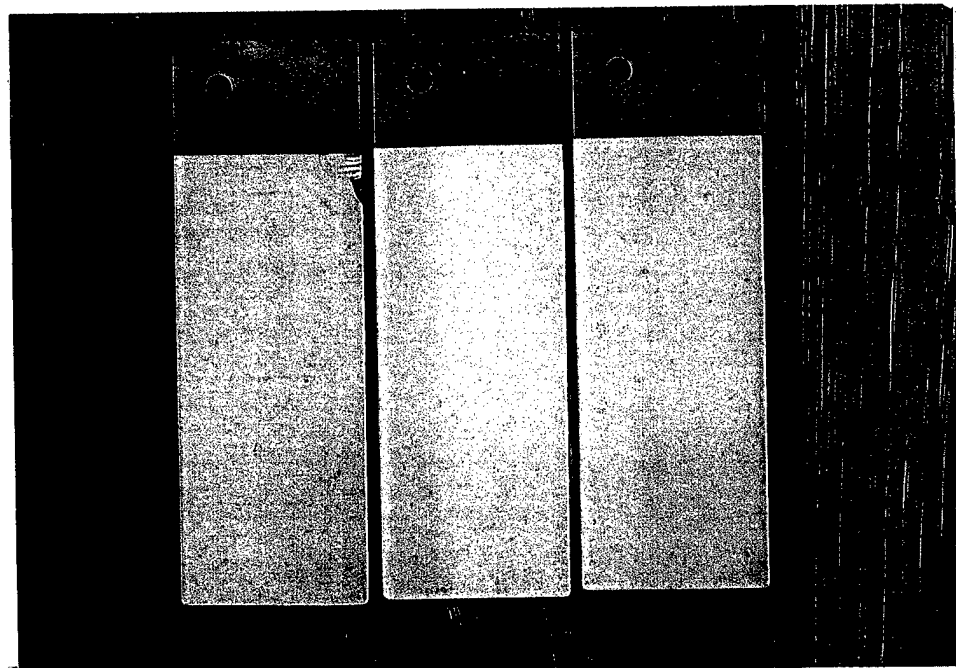


Figure 21.2 2609-04-019-22

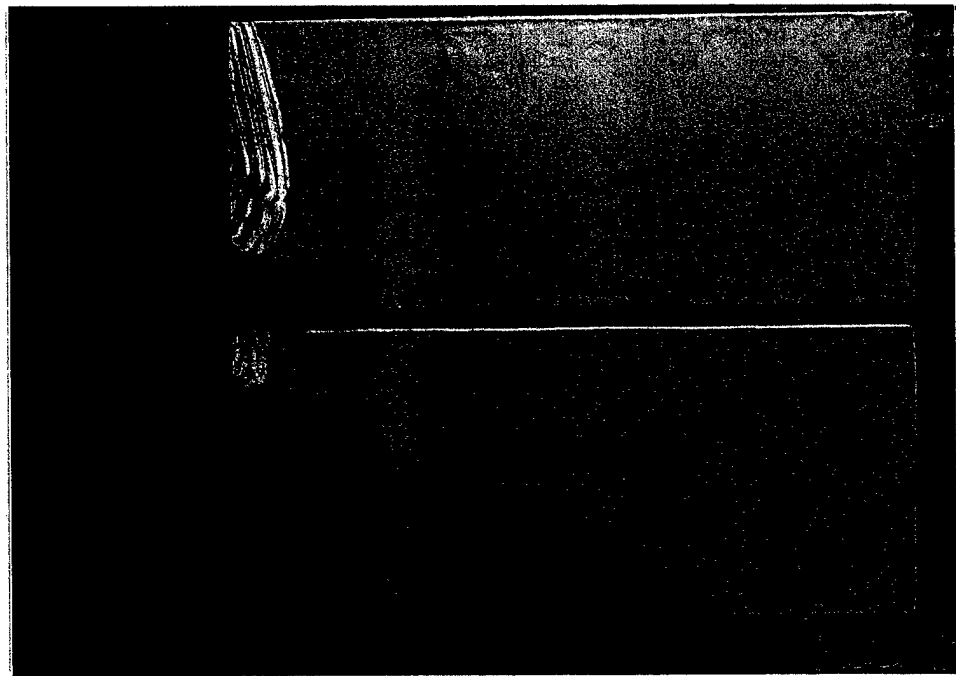


Figure 21.3 2609-04-023-14



Figure 22.1 2609-04-020-1

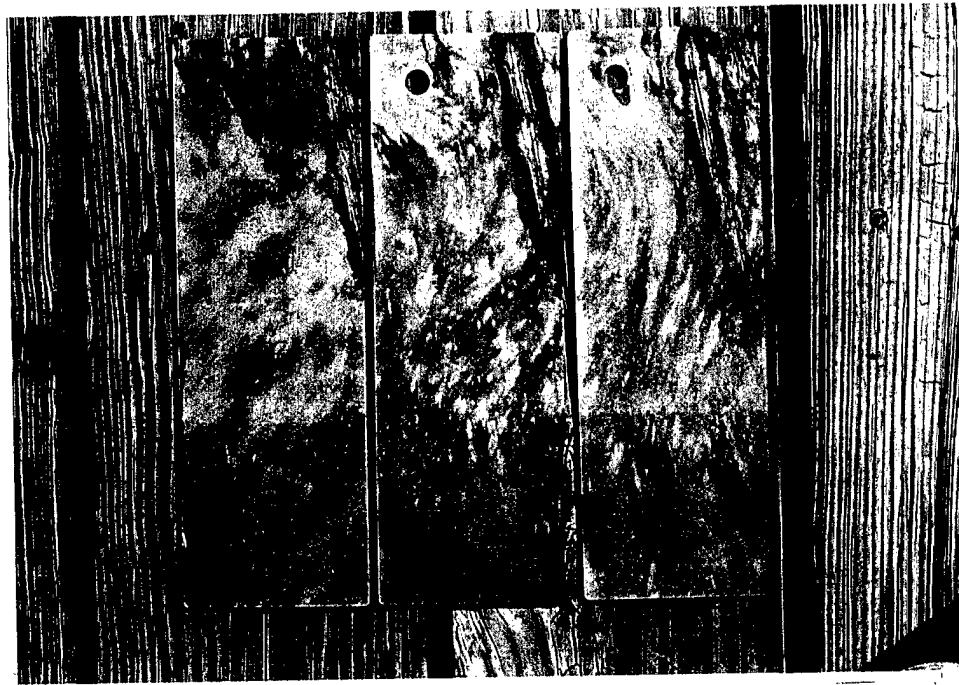


Figure 22.2 2609-04-020-7

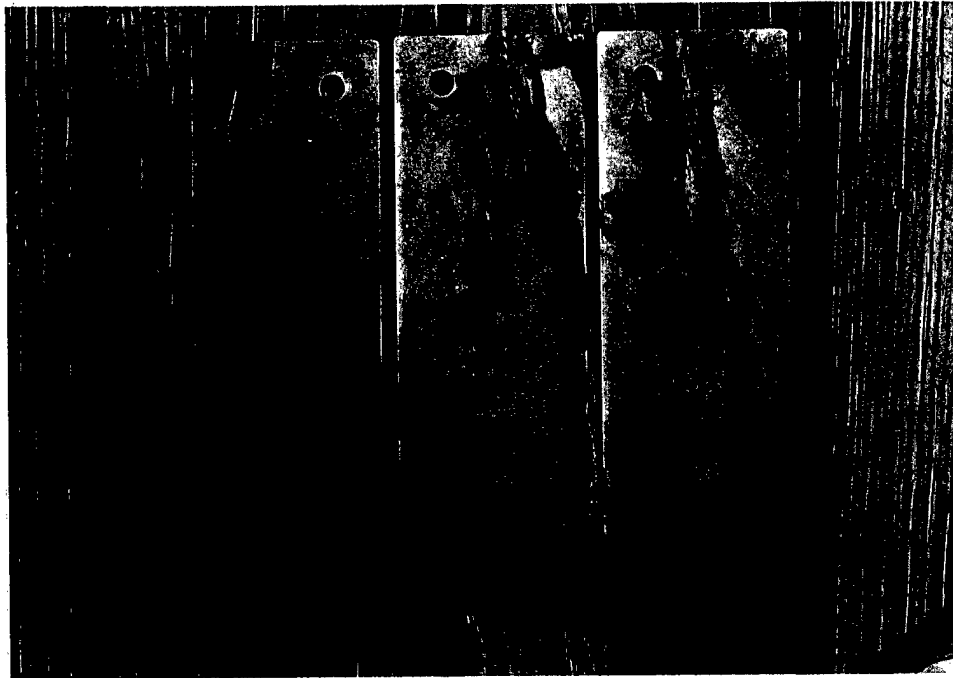


Figure 22.3 2609-04-020-13

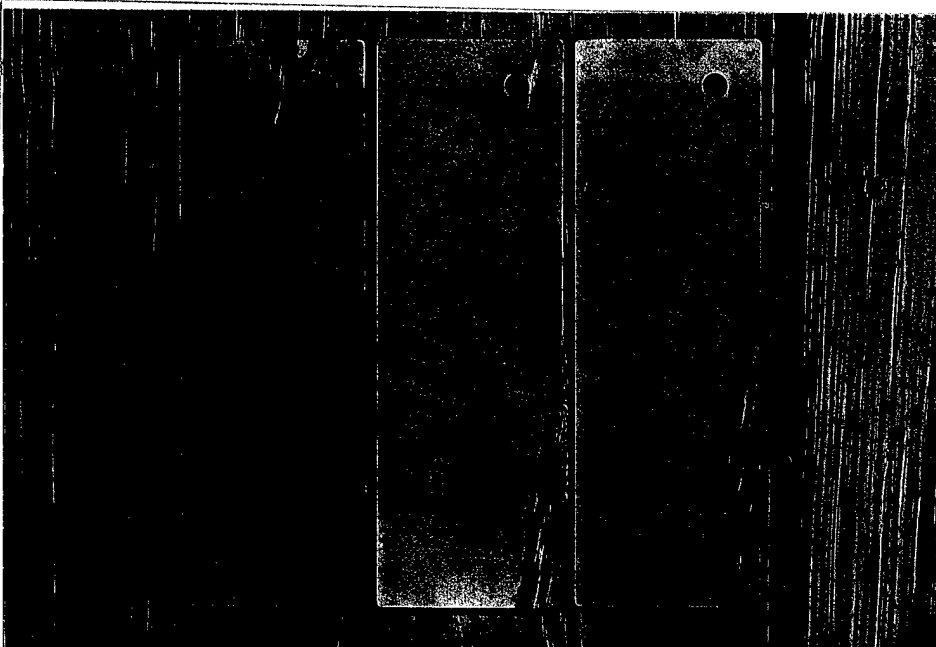


Figure 23.1 2609-04-020-4

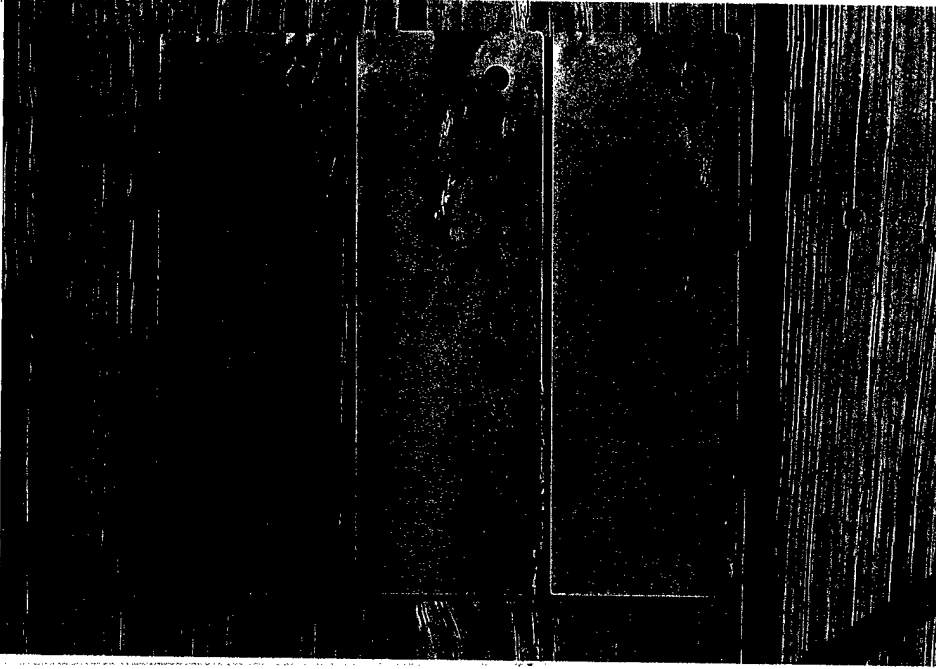


Figure 23.2 2609-04-020-10

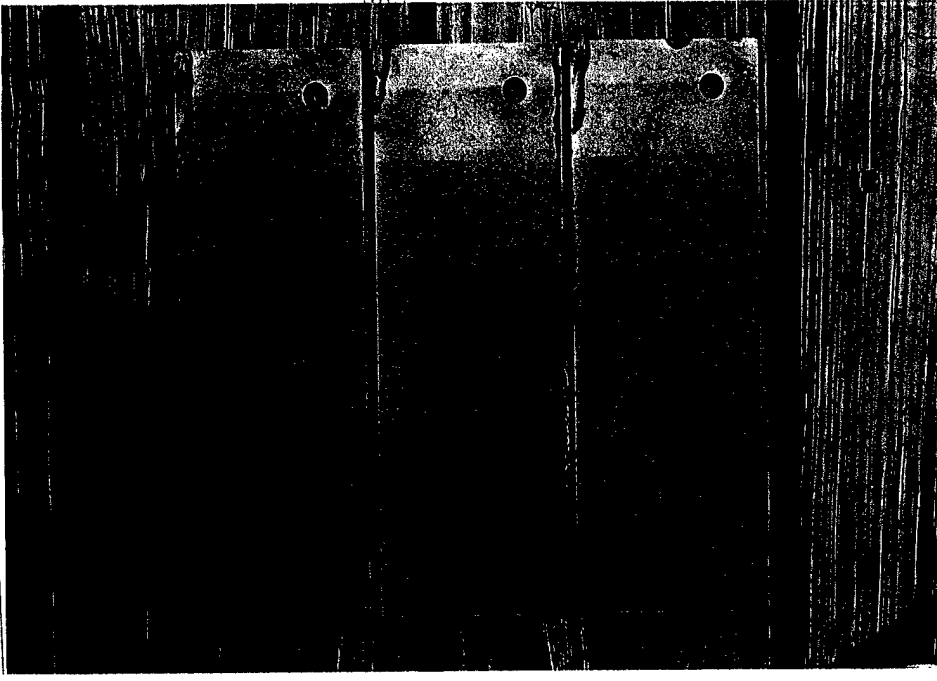


Figure 23.3 2609-04-020-16

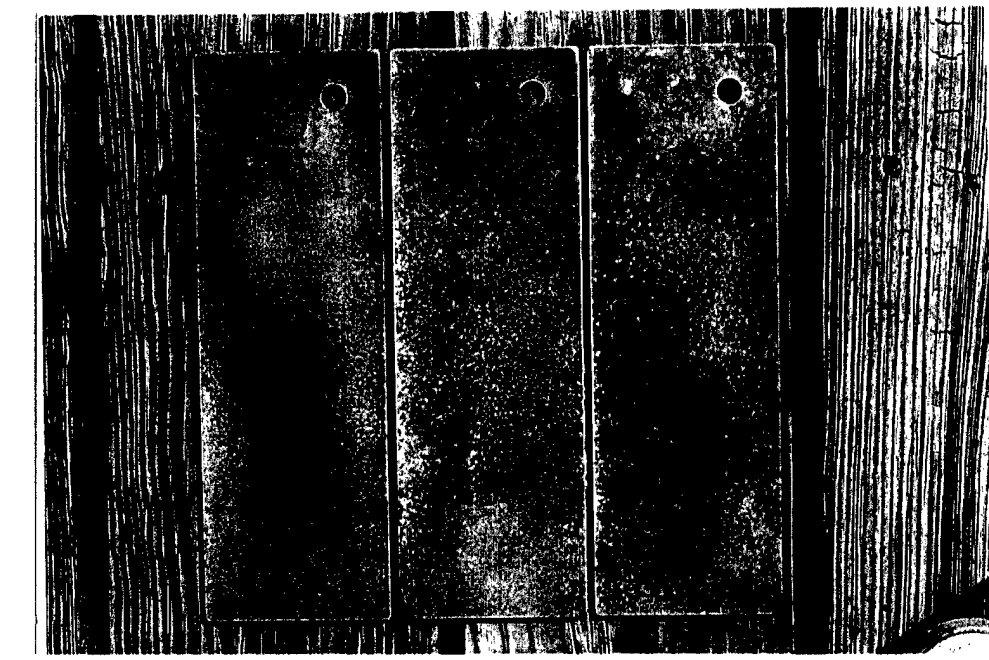


Figure 24.1 2609-04-020-19

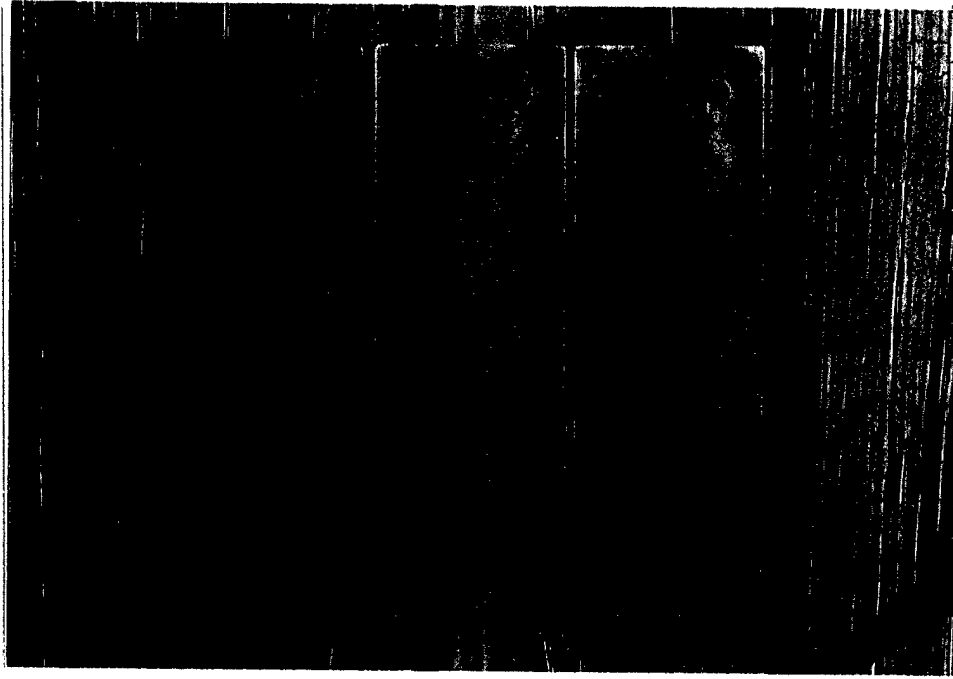


Figure 24.2 2609-04-021-1

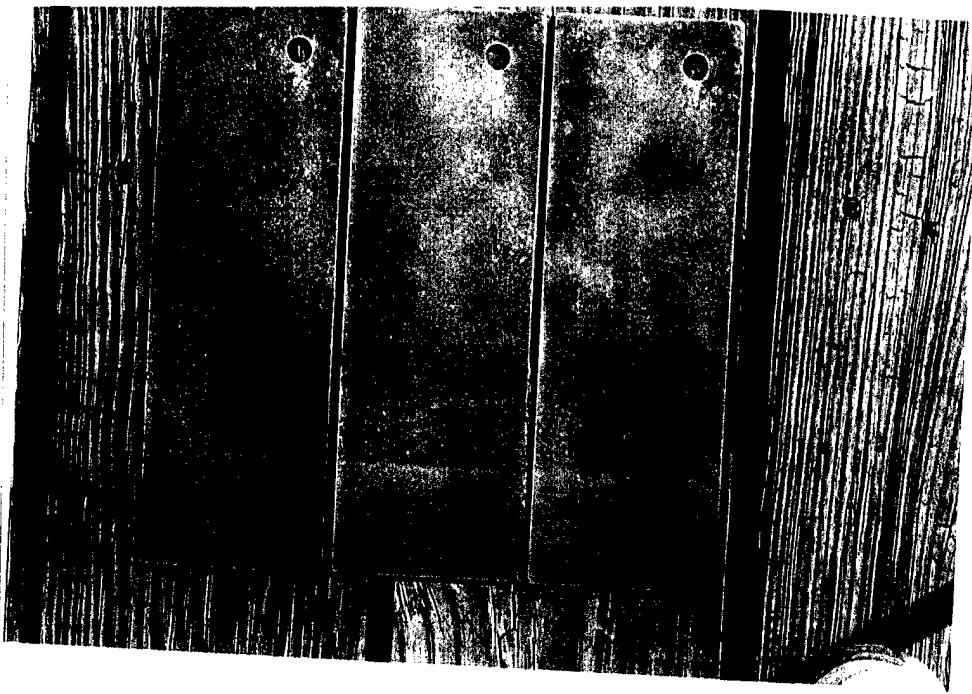


Figure 24.3 2609-04-021-7

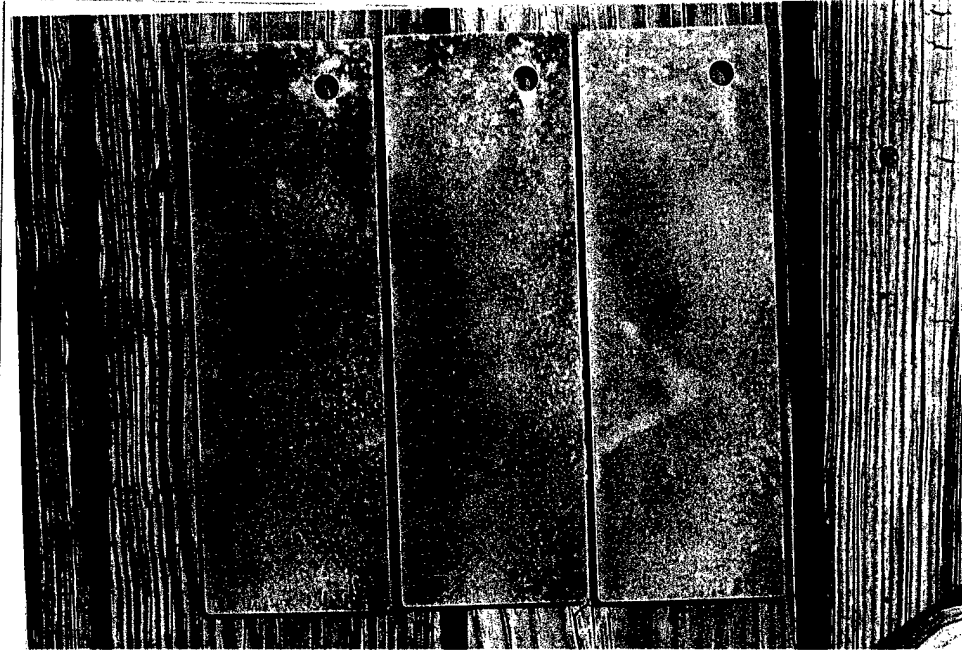


Figure 25.1 · 2609-04-020-22

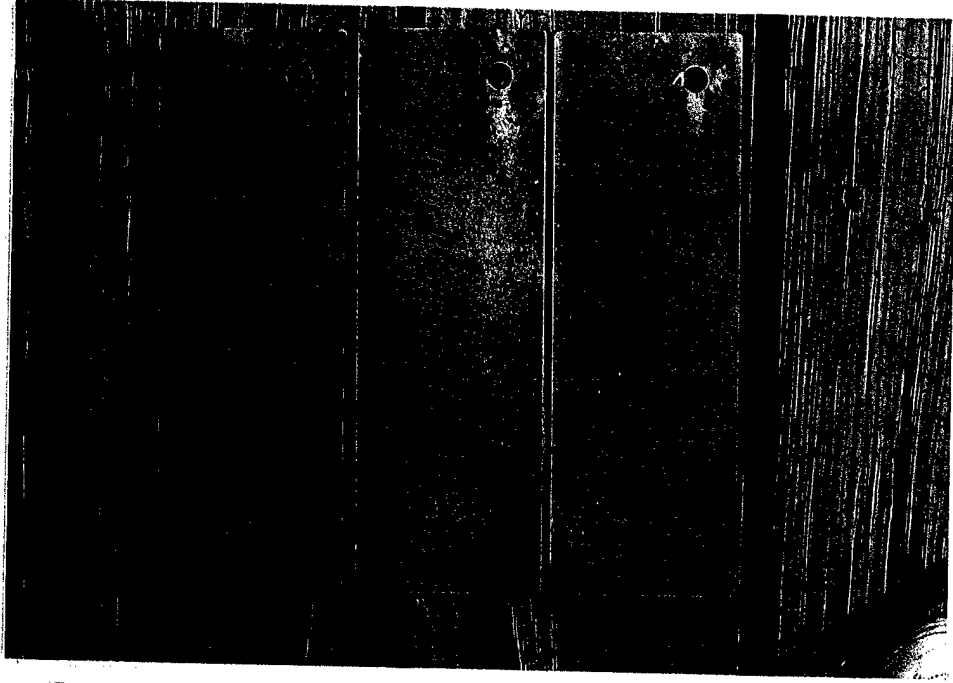


Figure 25.2 2609-04-021-4

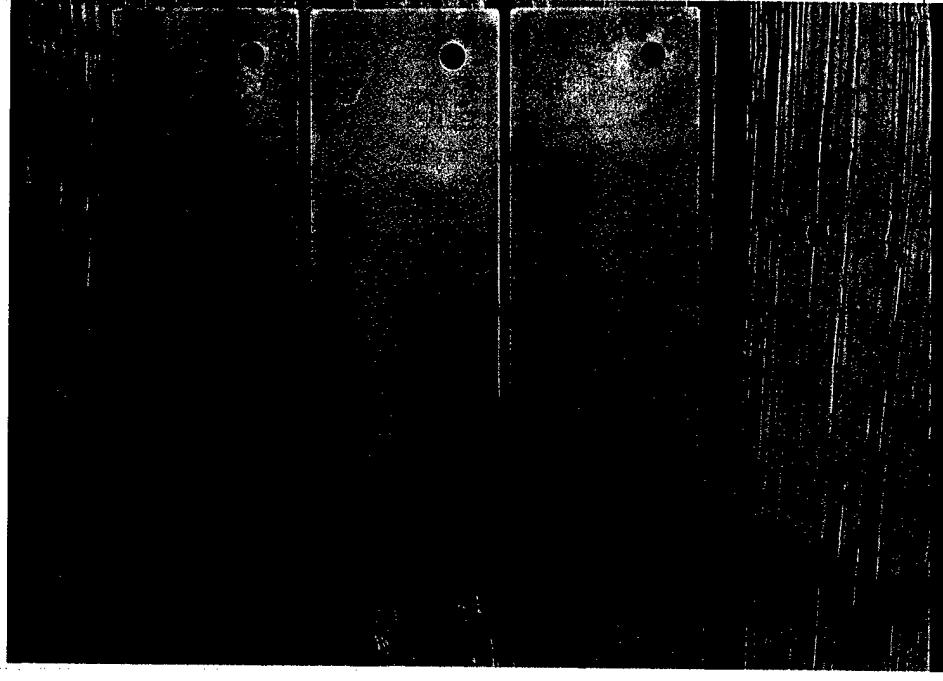


Figure 25.3 2609-04-021-10

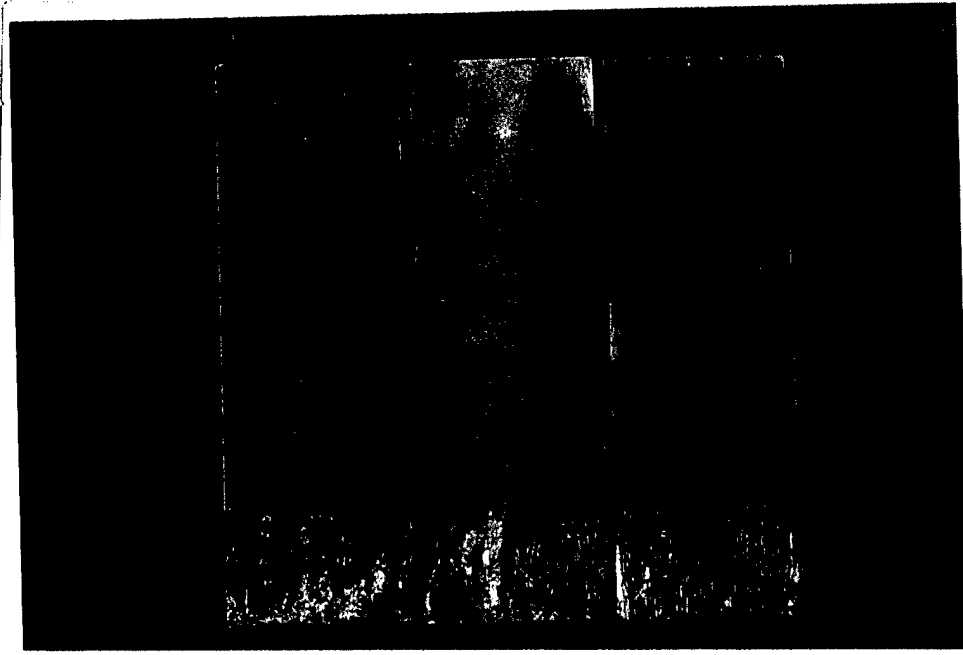


Figure 26.1 2609-04-018-10

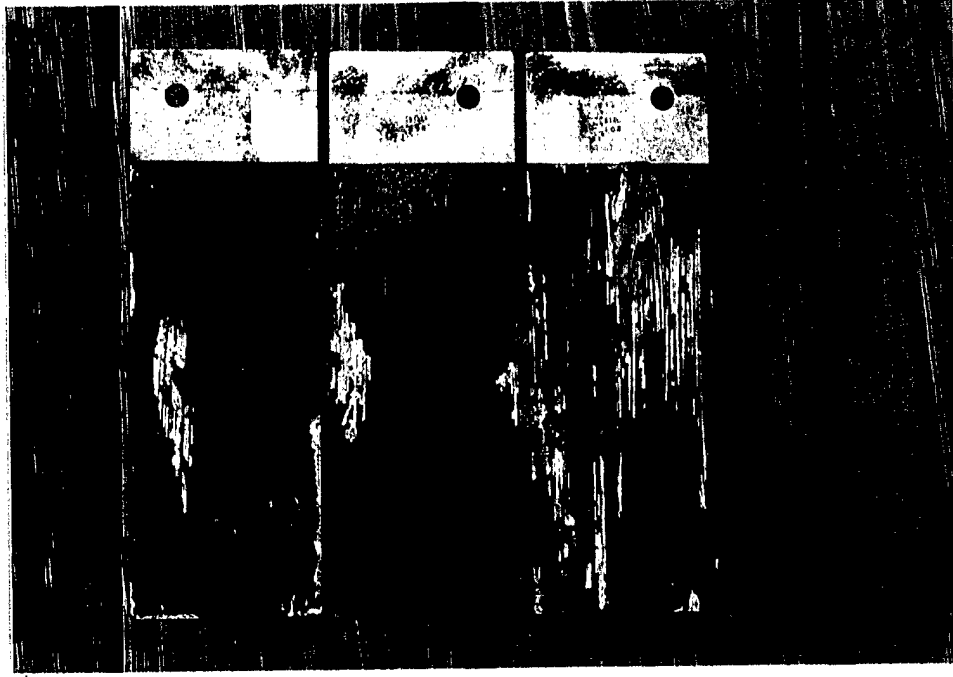


Figure 26.2 2609-04-018-13

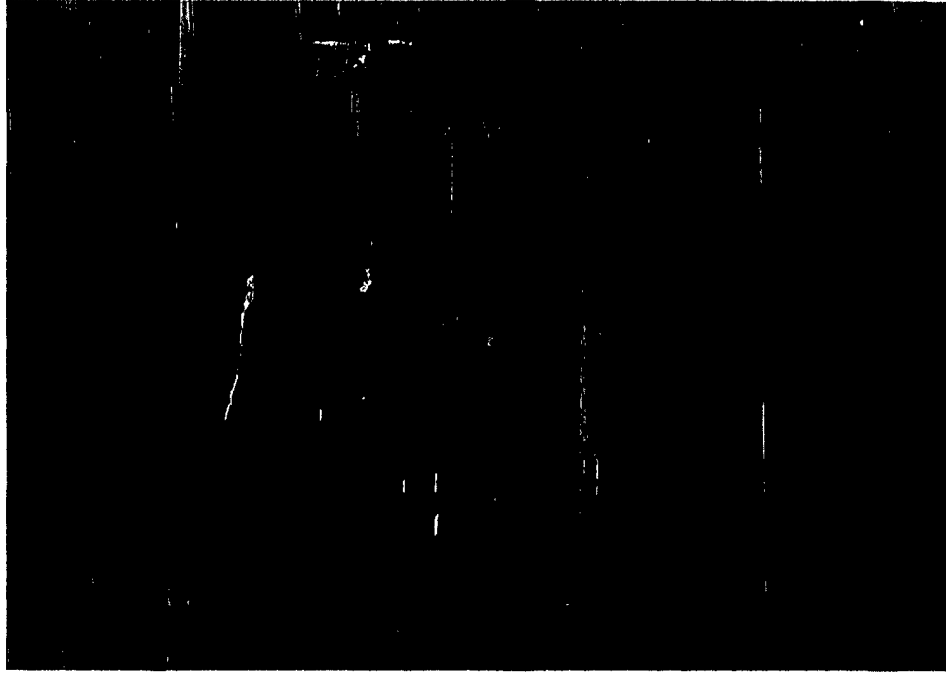


Figure 26.3 2609-04-018-16

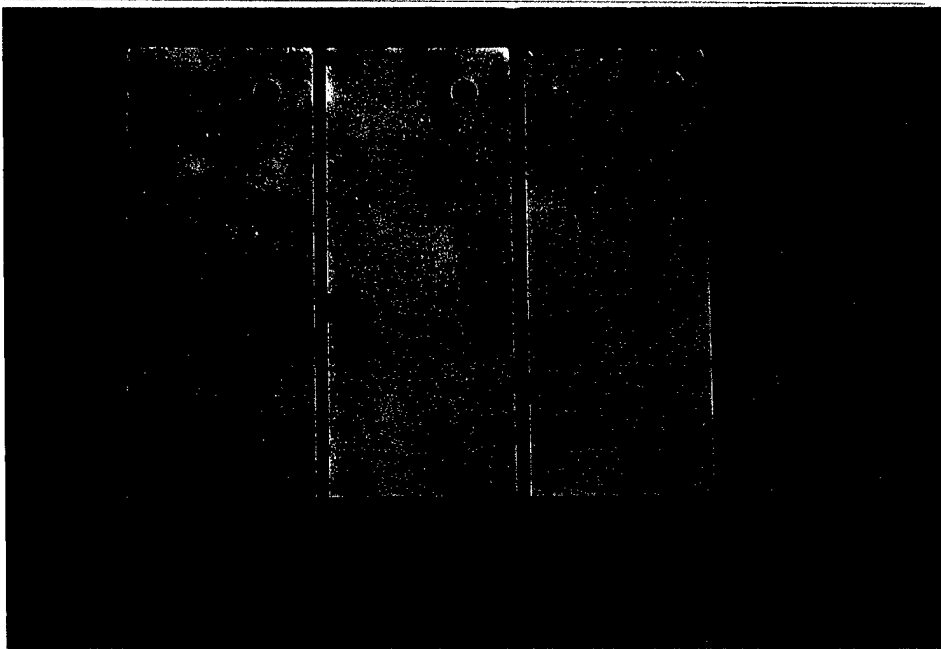


Figure 27.1 2609-04-018-1

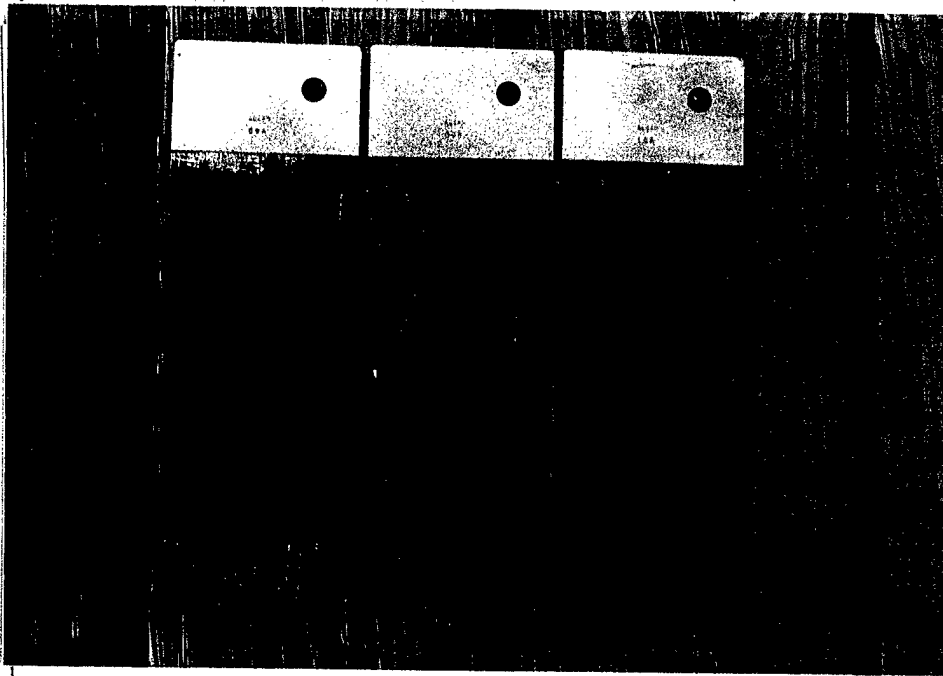


Figure 27.2 2609-04-018-4

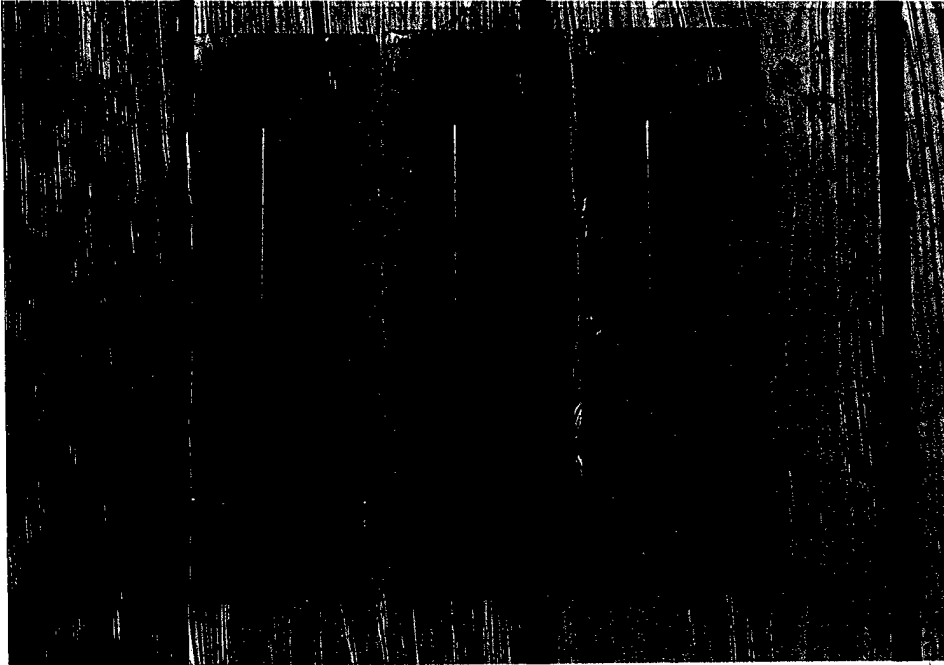


Figure 27.3 2609-04-018-7

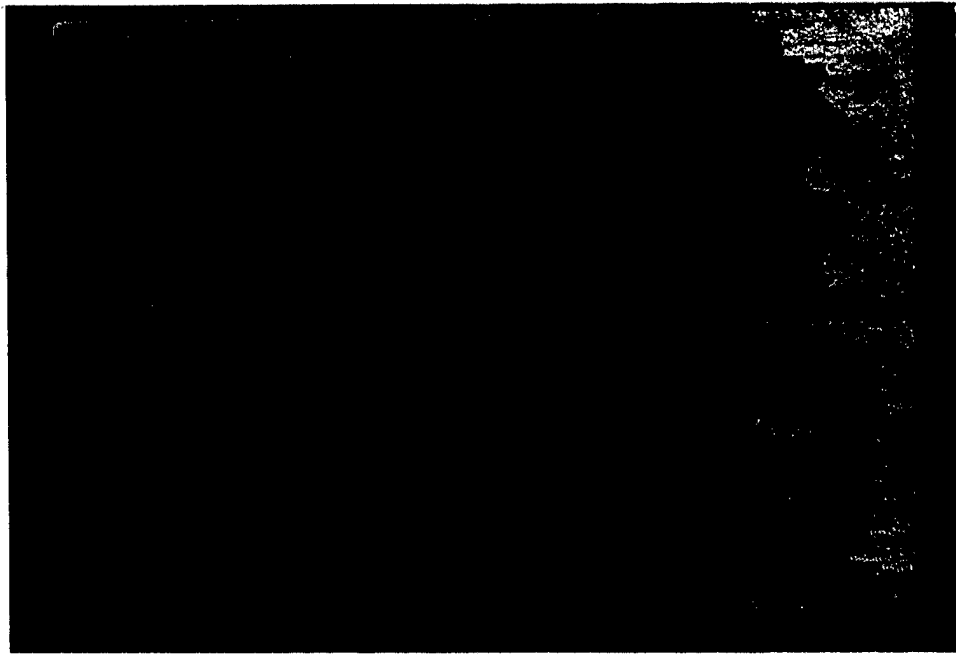


Figure 28.1 2609-04-022-2A

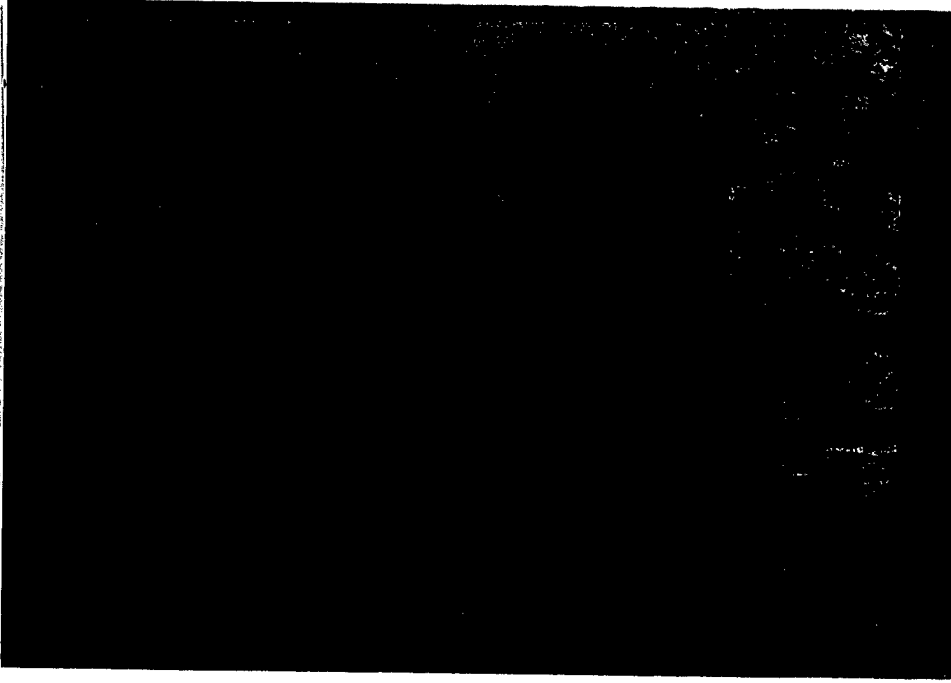


Figure 28.2 2609-04-022-8A

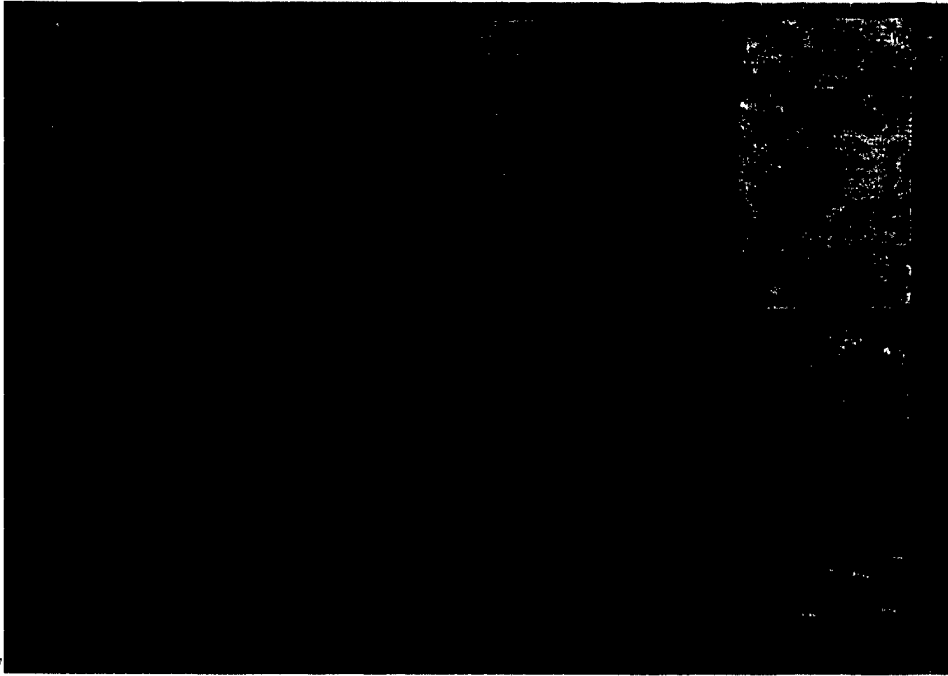


Figure 28.3 2609-04-022-14A

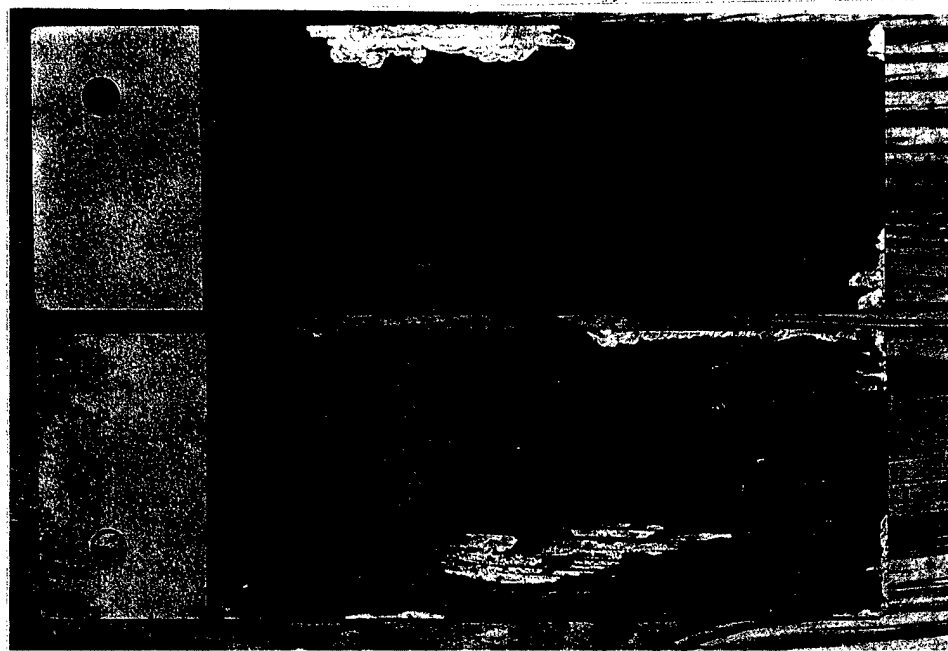


Figure 29.1 2609-04-022-5A

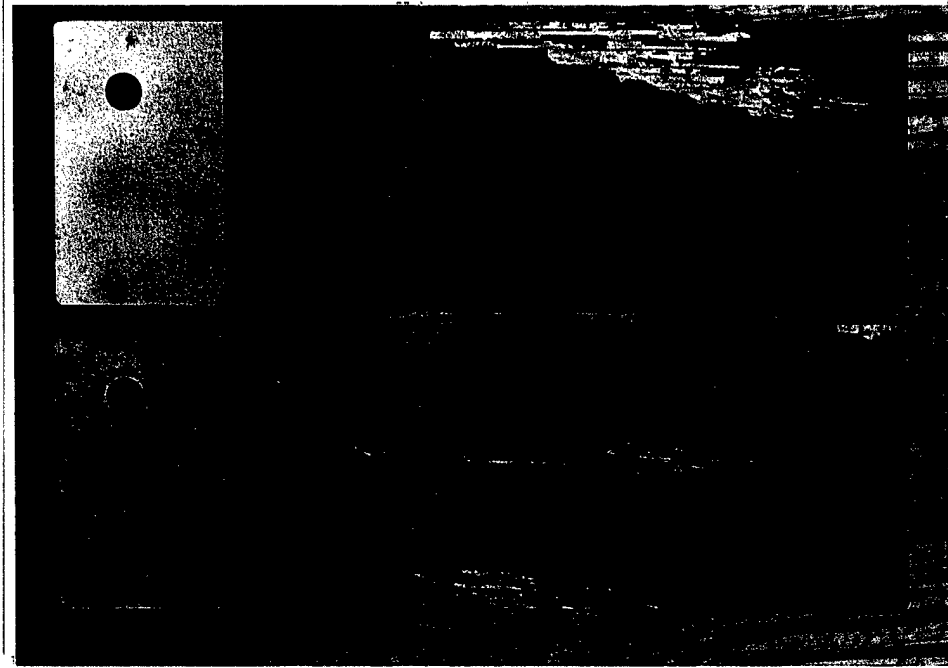


Figure 29.2 2609-04-022-11A



Figure 29.3 2609-04-022-17A

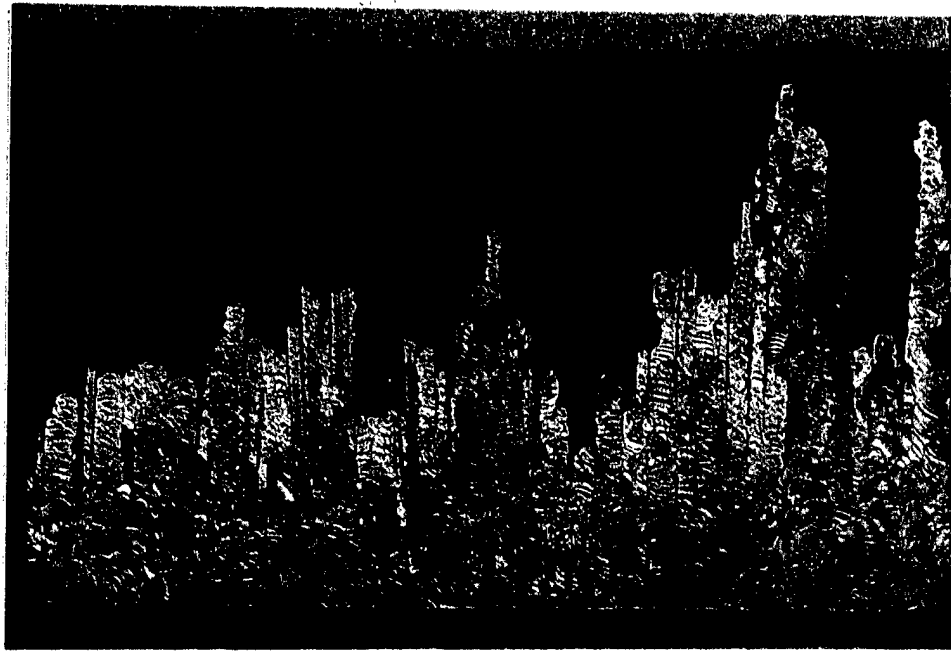


Figure 30.1 2609-04-024-20

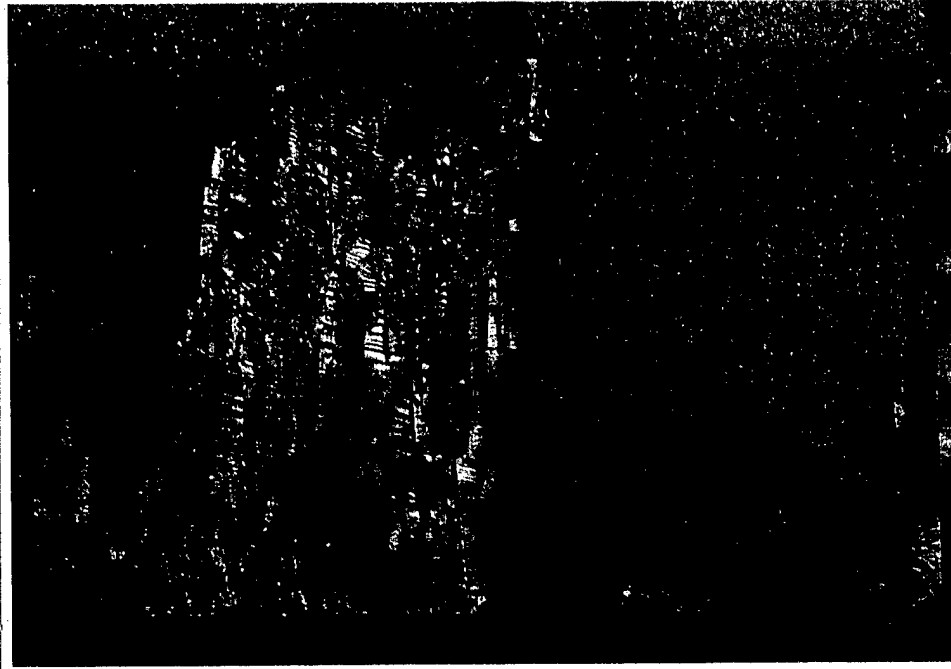


Figure 30.2 2609-04-025-2



Figure 30.3 2609-04-024-23

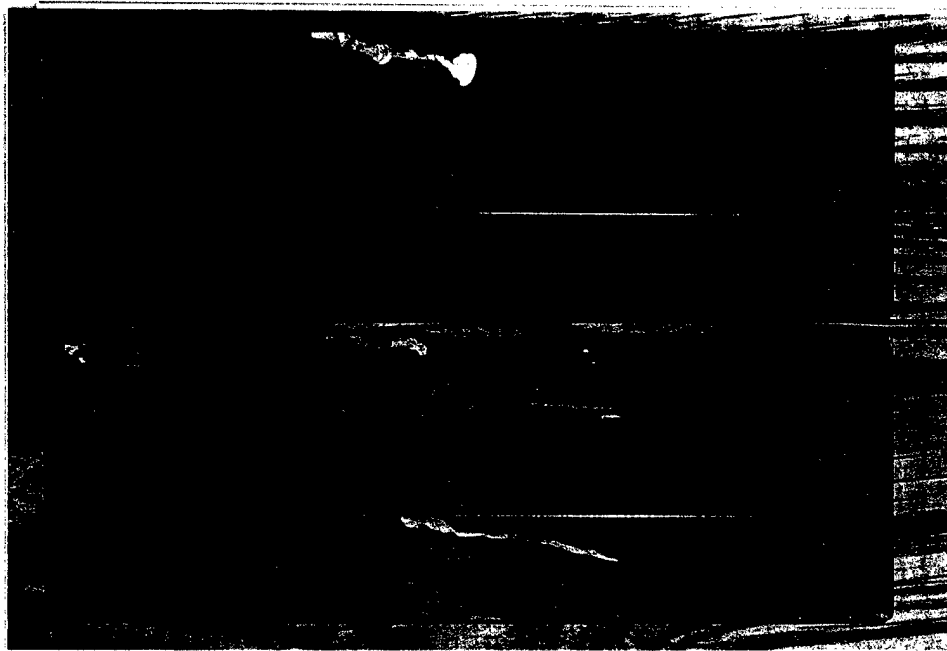


Figure 31.1 2609-04-022-20A

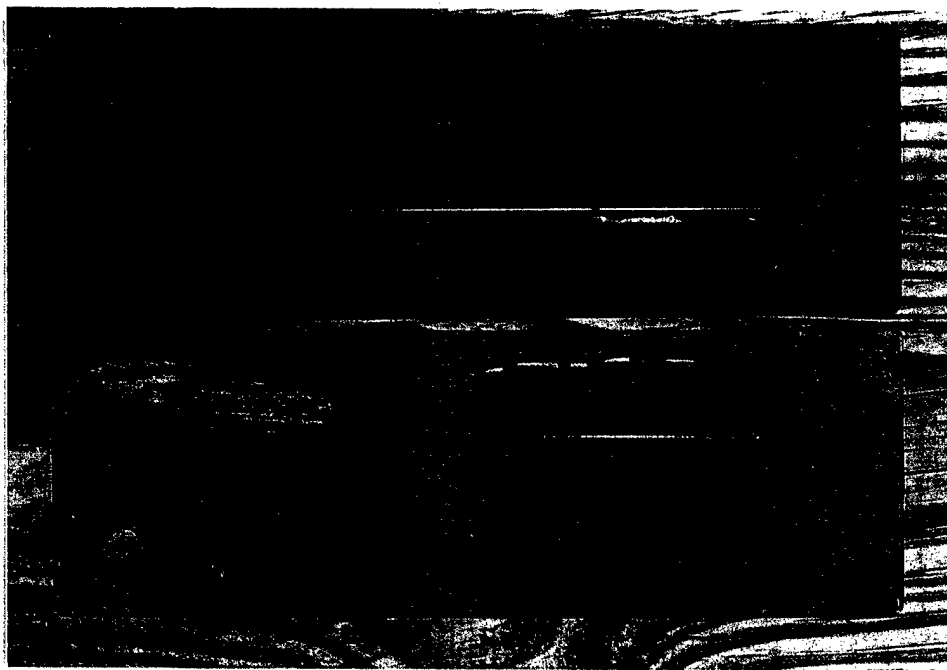


Figure 31.2 2609-04-022-23A

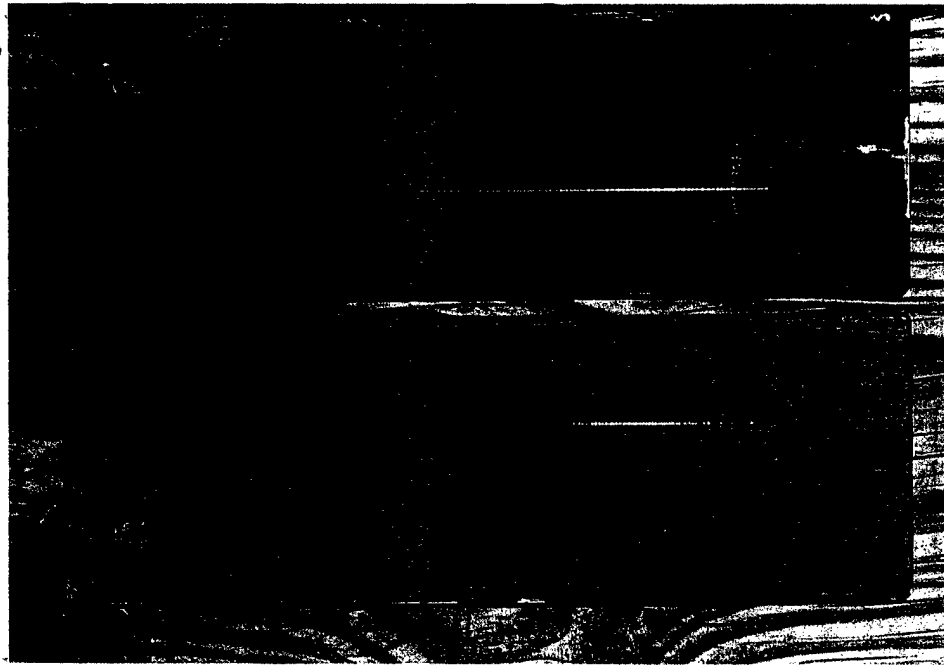


Figure 31.3 2609-04-023-2

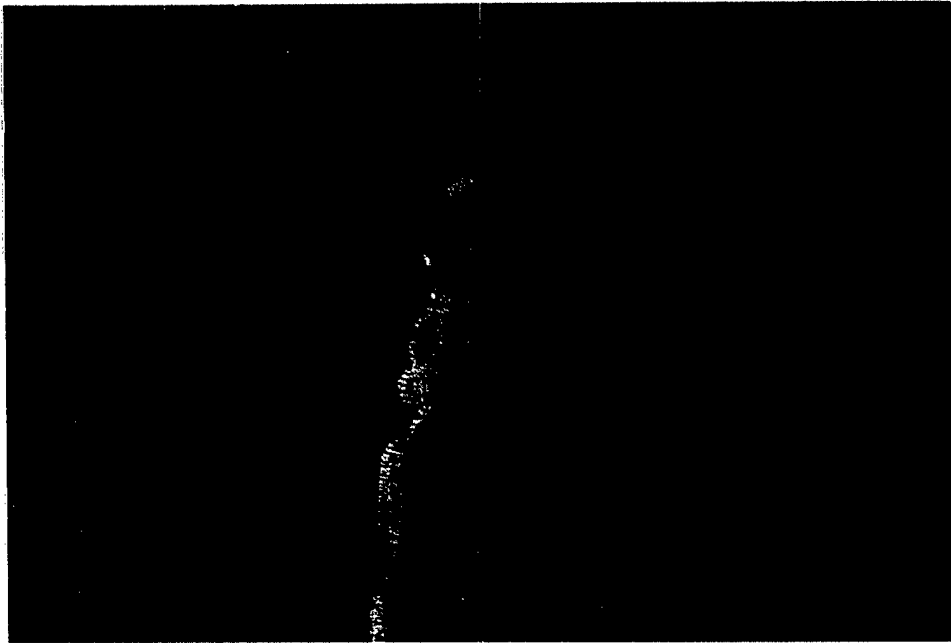


Figure 32.1 2609-04-024-17

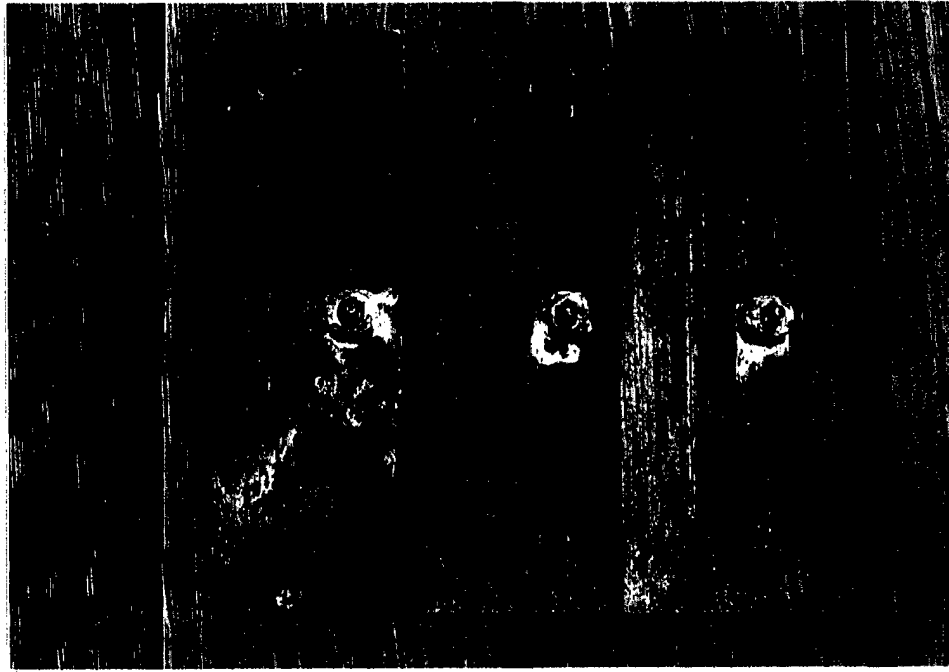


Figure 32.2 2609-04-018-19

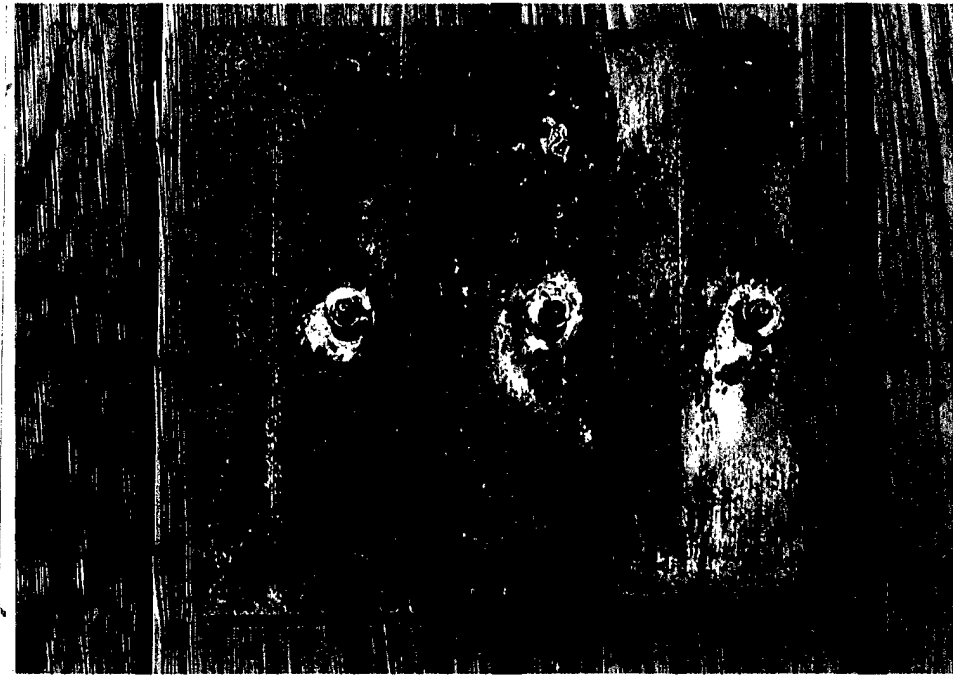


Figure 32.3 2609-04-018-22

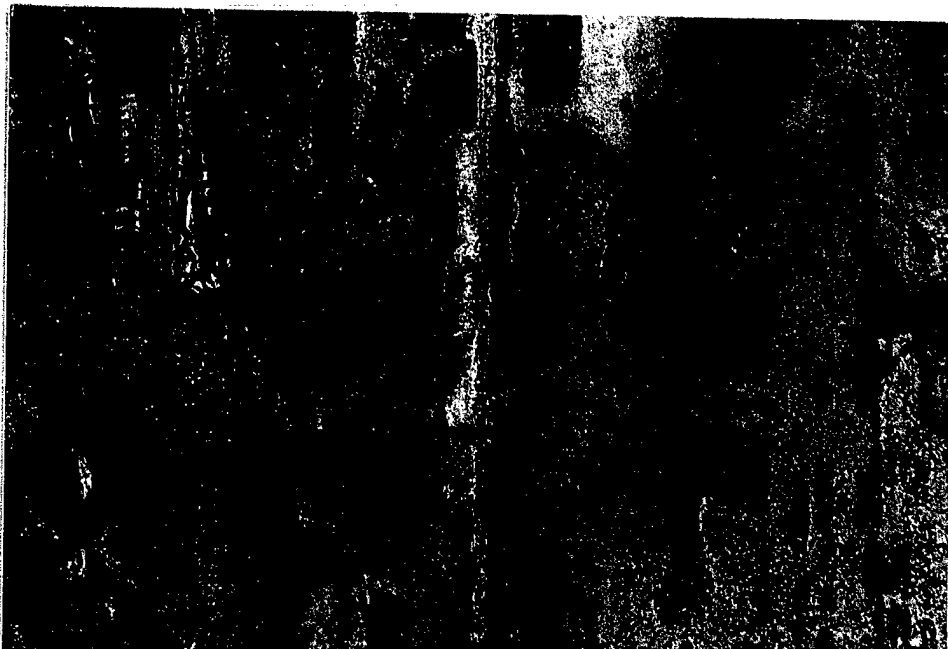


Figure 33.1 2609-04-024-14

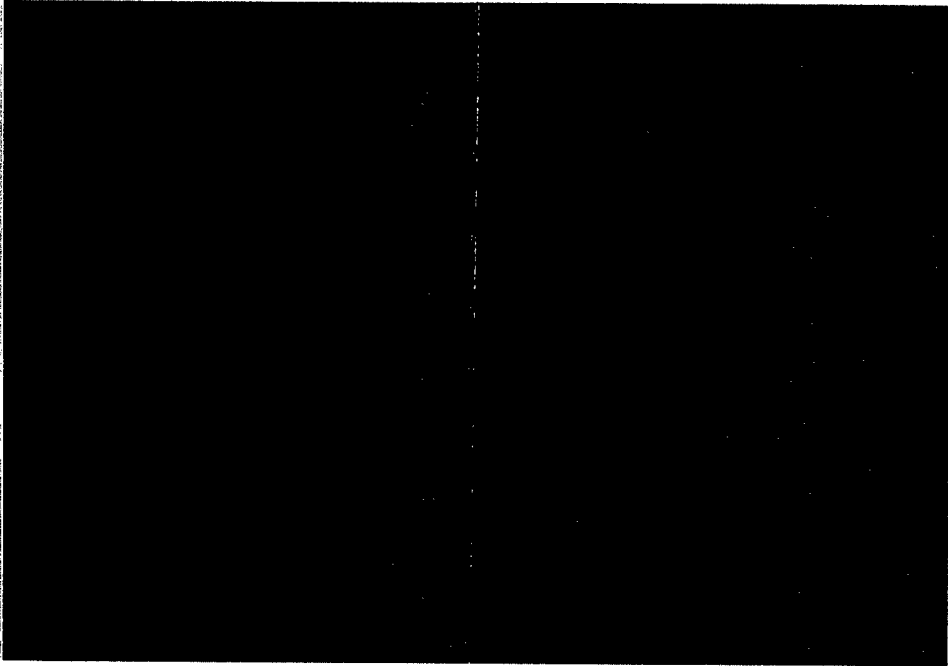


Figure 33.2 2609-04-024-8